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HONOLULU, HAWAII
Under the supervision of the
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52

BULLETIN No. 52

MANGANESE CHLOROSIS OF PINEAPPLES: ITS CAUSE AND CONTROL

BY

MAXWELL O. JOHNSON, Chemist

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[1] Resigned, effective Mar. 20, 1919.
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MAIN FIELD EXPERIMENT SHOWING BENEFITS PRODUCED WITH IRON SULPHATE SOLUTION. PLANTS ON LEFT NOT SPRAYED, THOSE ON RIGHT SPRAYED.

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MANGANESE CHLOROSIS OF PINEAPPLES: ITS CAUSE AND CONTROL.

By M. O. Johnson,[1] *Chemist.*

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YELLOWING OF PINEAPPLES ON MANGANESE SOILS.

The yellowing of pineapples grown on the manganese soils of the Hawaiian Islands was a serious problem to pineapple growers for many years. Large areas of these black or dark manganese soils are found in the chief pineapple-growing district lying on the sloping plateau between the Koolau and Waianae Mountain ranges on the island of Oahu. Such soils also occur in the very large potential pineapple areas on the islands of Molokai and Lanai, and to some extent on the islands of Kauai and Maui. None of these areas could be profitably utilized until a solution of the manganese problem was found.

When pineapple plantings were first being extensively made in 1902, prospective growers eagerly sought the dark soils, being influenced by the color which was thought to be indicative of great fertility. It was soon discovered that the pineapples on these soils suffered serious injury, a trouble which locally became known as "pineapple yellows," or "manganese yellows."

The most pronounced characteristic by which these pineapple plants were differentiated from normal plants was a gradual fading of the leaves until the whole plant assumed a yellowish-white appearance. Blanching of the leaves occurred at any period of growth, but usually started in three to six months after the time of planting.

[1] The writer wishes to thank J. M. Westgate, agronomist in charge of the Hawaii Agricultural Experiment Station, for heartiest support and encouragement in this investigation, and J. T. Whitmore, S. T. Hoyt, and H. Blomfield Brown, of the Hawaiian Pineapple Co., for their generous cooperation and help.

In many cases the plant ceased growth and began to die back from the tips of the leaves. During the earlier stages of development the fruit was reddish-pink in color instead of deep green, and in the ripened stage the flesh was not only hard and white instead of straw-colored, but it also lacked flavor and contained considerable acid. Many of the fruits cracked open and decayed before ripening.

Preliminary reports (*24*, *25*, *26*) [2] of the writer's investigations on the manganese problem were published in order to make available as quickly as possible information concerning the simple remedy discovered for the "manganese yellows." This remedy, consisting of inexpensive sprayings with solutions of iron sulphate, met with immediate success and is now being used on thousands of acres of Hawaiian pineapples. Considerably over half of Hawaii's production of canned pineapples is borne by sprayed plants. This bulletin gives a rather detailed account of the results obtained and also of the manner in which manganese induces chlorosis.

REVIEW OF PREVIOUS INVESTIGATIONS ON MANGANESE.

Manganese is found in small quantities in most soils and in many plants. Certain forest trees, notably the conifers, contain rather large amounts of manganese. Schroeder (*40*, *41*) reported in 1878 the occurrence of 35.53 per cent Mn_3O_4 in the ash of pine needles and of 41.23 per cent in the ash of pine bark. Many experiments have been made with manganese in different forms as a fertilizer. Kelley (*32*) and Skinner and Sullivan (*43*) give extensive reviews of these experiments. It is not necessary to refer to these in detail, as they were carried on in connection with crop production, and the results obtained do not show that manganese is valuable as a fertilizer. Some investigators have found a stimulation of growth from the application of small quantities of various manganese compounds, while others have found no effects and even a retardation of growth. It appears generally that the application of large amounts of manganese produces a toxic effect.

The chemical similarity of manganese and iron has suggested a number of interesting experiments dealing with the physiological effects of manganese. Unsuccessful attempts were made by Sachs (*38*), Birner and Lucanus (*7*), and Wagner (*45*) to substitute manganese for iron in the production of chlorophyll, and an injurious effect was noted when manganous and manganic phosphates were suspended in culture solutions.

Since the discovery by Bertrand (*5*, *6*) that manganese occurs in the ash of oxidizing enzyms, the physiological effects of manganese on plants have been generally attributed to some influence of the manganese on these enzyms.

Loew and Sawa (*33*) in 1902 observed a yellowing of pea plants, barley, and soy beans in water-culture experiments with solutions to which small amounts of manganese sulphate had been added. The addition of manganese sulphate to the usual iron-containing nutrient solution caused an increased growth in which yellowing later took place. This yellowing is thought to have been due to the increased activity of the oxidizing enzyms. They conclude that "manganese exerts in moderate quantity an injurious action on plants, consisting

[2] Reference is made by number (italic) to "Literature cited," p. 36.

in the bleaching out of the chlorophyll. The juices of such plants show more intense reactions for oxidase and peroxidase than the healthy control plants."

Aso (*1*) in similar water cultures with young radish, barley, and wheat plants observed a yellowing with solutions containing (*a*) 0.02 per cent $MnSO_4$ + trace of $FeSO_4$, (*b*) 0.02 per cent $MnSO_4$ + 0.02 per cent $FeSO_4$ in comparison with (*c*) 0.02 per cent $FeSO_4$ and in these three solutions diluted with 10 times their volume of water. The ordinary mineral constituents were supplied. When the solution containing manganese sulphate and only a trace of ferrous sulphate was diluted 10 times the yellowing suggested a lack of iron. Pea shoots grown during the first stage of development in solutions containing no mineral salts and only 0.002 per cent ferrous sulphate and manganous sulphate singly and in combination found the greatest stimulation with the manganous sulphate. No yellowing was observed during this first stage of development. Aso concludes that:

(1) Manganese salts exert on the one hand an injurious action and on the other a stimulant influence on plants; with increased dilution the former diminishes while the latter increases. Thus a dilution can be reached in which only the favorable action of manganese becomes obvious.

(2) Manganous sulphate added in a dilution of 0.002 per cent to culture solutions exerted a stimulant action upon radish, barley, wheat, and pea. Iron seems to counteract to a certain degree the action of the manganese.

(3) The intensity of the color reactions of the oxidizing enzyms of the manganese plants exceeds that of the control plants.

That the injurious effects of manganese may be due to a depressed assimilation of iron does not appear to be suspected in the later work of Aso (*2*, *3*) and other investigators.

Katayama (*27*) found an increase in yield of barley when small amounts of manganous sulphate were used. Large amounts of manganese retarded growth.

In 1907 Salomone (*39*) published the results of an extensive investigation with various salts and oxids of manganese. A slight yellowing was observed in wheat in field experiments when small quantities of the oxids were used, but the final yield was increased. Serious injury was observed when manganese as manganous sulphate was applied at a rate greater than 50 kilograms per hectare, and the plants died when still larger quantities were used. The toxic effects, due to manganese, seem to be similar to those which the pineapple plant suffers on manganiferous soil, i. e., a yellowing, disorganization of the chlorophyll bodies, and other physiological derangements. The crop was injured also when these plats were planted to wheat for the second time. It is significant that lime and basic slag applications did not diminish this toxic effect as was also the case in the liming experiments on the manganiferous soils of Oahu.

Salomone also found that heavy applications of various manganese compounds caused the death of bean plants which were grown in boxes and that the toxicity of manganese was greater where manganese functioned as an electronegative element.

Hall (*21*) thinks that in field experiments the stimulating action of manganese is due to some indirect effect on the dormant bases of the soil rather than to a direct effect of the manganese. He does not, however, consider this point established.

Bernardini (*4*) in 1910 concluded from a series of experiments that manganese has a catalytic effect on soils, increasing their oxygen-absorbing power and possibly influencing the soil bacteria. Judging from the results of various experiments in which solutions of manganous chlorid effected replacement of large amounts of lime and magnesia in certain silicates, he thinks that the stimulating effect of applied manganese may be due to some indirect effect of replacement rather than to any physiological action.

Brenchley (*8*) in water cultures of barley found a stimulating effect with very small amounts of manganous sulphate, but noted that the plants turned brown and died with large quantities.

Kelley (*28, 29, 30, 31*) was the first to publish results showing that there is a close correlation between the yellowing of pineapples in Hawaii and an abnormal amount of manganese in the soil.

Wilcox and Kelley (*46*) found, in their study of the effects of manganese on pineapple plants and the ripening of the fruits, that sections showed under the microscope a fading of the chlorophyll and a destruction of the organized structure of the chloroplasts.

In 1912 Kelley (*32*) published the results of an extensive investigation of the effects of these manganiferous soils of Oahu on the pineapple and other plants. Notes were made comparing the appearance and growth of field plants in manganiferous soil with plants in normal soil, and likewise of plants in pots of manganese soil with those in pots of normal soil.

From this investigation Kelley concluded that—

> Various plants when grown on manganiferous soil are affected differently. Some species are stunted in growth and die back from the tips of the leaves, which turn yellow or brown and frequently fall off, and a general unhealthy appearance results. Other species appear to be unaffected and so far as can be judged vegetate normally in the presence of manganese. Microscopic investigations have shown that in certain instances the protoplasm undergoes changes. Occasionally it draws away from the cell walls, the nuclei become brown, and plasmolysis takes place. * * *
>
> From the ash analysis it was found that manganese was absorbed in considerable quantities, and in nearly every instance was greater in the plants from manganiferous soil. The ash analysis also shows that a disturbance of the mineral balance takes place. The percentage of lime is increased, while the absorption of magnesia and phosphoric acid is decreased. * * *
>
> From these evidences we may believe that the effects of manganese are largely indirect and are to be explained on the basis of its bringing about a modification in the osmotic absorption of lime and magnesia, and that the toxic effects are chiefly brought about through this modification, rather than as a direct effect of the manganese itself.

In 1914 Skinner and Sullivan et al. (*43*) published results of pot and field experiments in which compounds of manganese were applied as fertilizers. Changes were observed in the oxidative power of the soils as a result of the manganese. Manganese in small quantities had a stimulating effect in pot experiments with an unproductive soil, but resulted in no increase in growth with a productive soil. A five-year field test with an acid soil to which manganous sulphate was added at the rate of 50 pounds per acre showed a harmful effect on each of the crops grown. In regard to the toxic effects of large amounts of manganese, Skinner and Sullivan made the following statement:

> Where manganese has been of little value or has given decreased yields, conditions were such that stimulating actions on plant and microorganisms did not come into play, or, on account of the acid reaction of the soil, the effect of the

stimulation led to reduction processes being predominant. Large applications of manganese have been found injurious, undoubtedly because of excessive stimulation and excessive oxidation in microorganisms and in the plant, with a resulting change in the biochemical activities of plant and microorganisms and in the conditions of inorganic and organic soil constituents, the ultimate result of which change is injurious to the growing crop.

Later in 1916, Skinner and Reid (*42*) found that the productivity of the soil was increased by manganese when the plats on which the experiments were conducted were limed. They state that—

> The action of manganese in the acid soil was probably to stimulate the life processes in the soil, acting on the organic matter in such a way as to produce changes which resulted in a lessened crop-producing power, while its action in the neutralized soil was such as to stimulate oxidation and other biological processes, acting on the organic soil constituents and producing changes favorable to the growing plants.

Pugliese (*37*) from water-culture experiments similar to those of Loew and Sawa suspected an antagonism between iron and manganese and stated that there was an optimum ratio which he gave as 1 : 2.5.

McCool (*36*) found that—

> Pure solutions of manganese salts are extremely poisonous to pea and wheat seedlings. The degree of toxicity is greatly reduced by full nutrient solutions and by soil cultures. The injurious action of the manganese ion is manifested mainly toward the tops of plants. Chlorosis of the leaves is the first indication of an overdose of manganese. Manganese is less injurious to plants grown in the dark than to those grown in the light. Calcium, potassium, sodium, and magnesium ions are each effective in counteracting the poisonous action of manganese. Mutual antagonism exists between the manganese ion and each of the following: Potassium, sodium, and magnesium.

Tottingham and Beck (*44*) suspected an antagonism toward iron similar to those stated above for potassium, sodium, and magnesium.

Brown and Minges (*9*) in 1916 believed that the effects of manganese applications to the soil may be ascribed to their effect on ammonification and nitrification.

Funchess (*13*) found that the nitrification of dried blood on certain Alabama soils produced soluble manganese salts which were toxic in effect.

Deatrick (*12*) found in high concentrations that manganese salts exerted a toxic effect, and in lower concentrations marked stimulation. "The toxic influence results in the browning of the roots and the bleaching of the leaves."

PREVIOUS INVESTIGATIONS ON LIME-INDUCED CHLOROSIS.

It has been known for many years that some plants become affected with chlorosis or bleaching when they are grown on soils containing very large amounts of carbonate of lime. Some species of grapevines which grow on certain highly calcareous soils of France are probably the best-known examples of chlorosis. This bleaching has been attributed by some investigators to lack of potash in the soil or to the physical condition of the soil, but the general conclusion seems to be that the condition is brought about by lack of iron in the plants, due to excessive amounts of carbonate of lime in the soil. Manganese has not been associated with this condition.

Gile and Ageton (*16*) have probably made the latest and most thorough investigation of such highly calcareous soils. In 1911 Gile

(*15*) found chlorosis to occur on certain areas of Porto Rican soils and attributed it to an excessive amount of carbonate of lime in the soil. In this connection Gile notes that—

> Chlorosis (sometimes called icterus, bleaching, or Gelbsucht) is the term applied to that condition assumed by the leaves of plants when they fail to develop the normal amount of chlorophyll, or green coloring matter, i. e., when they are yellowish or white instead of a normal green. Chlorosis, then, does not denote a specific disease, but merely a general condition. This condition of chlorosis, however, is the result or outward sign of a disease or disturbance in the physiology of the plant. To say that a plant is chlorotic or affected with chlorosis means merely that its leaves are lacking in chlorophyll; but the chlorosis may have resulted from a bacterial disease, poor drainage, lack of nutriment, or some other cause.

Bleaching was found to occur on soils very high in calcium carbonate while healthy plants were found on a soil containing 1.14 per cent calcium carbonate and a total lime content of 1.92 per cent. Manganese is not associated by Gile with this chlorosis as no manganese is reported as present in the soils or in the plants. Bleaching in this case appeared to be somewhat different from the yellowing of pineapples which occurs on manganiferous soils. Although a few cases of yellowing are noted, the typical appearance described is that of "waxy white" or "ivory white." No mention is made of the very characteristic red fruit which appears on manganiferous soils. The application of stable manure was found to be ineffective on these calcareous soils.

In this, as in previous cases of chlorosis which were induced by lack of iron in plants growing on highly calcareous soils, Gile found that the plants were benefited when the leaves were brushed with iron salts in solution, but that the treatment was impracticable for Porto Rican conditions. Gile (*15*, p. 34) states that—

> It is very doubtful if treatment with iron salts would render pineapple growing on calcareous soils commercially successful, as the repeated treatments with iron would be expensive and the crop would not be equal to that secured from soils naturally adapted to pineapples.

STATUS OF THE MANGANESE PROBLEM WHEN THE PRESENT INVESTIGATIONS WERE UNDERTAKEN.

From a review of the literature on manganese, it appears that the results and conclusions concerning the effect of this element on plants are very contradictory. Manganese is commonly thought to exert a stimulating action, but there seems to be no positive proof that such stimulation is due primarily to manganese. The experiments in soil culture are so contradictory that the stimulative effects found may be considered due to the effect of the anion, usually the sulphate, which is known to cause decided stimulation, particularly on alkaline soils. The possibility of manganese being a necessary element is sometimes discussed because of its occurrence in the ash of plants. Aluminum also is found in the ash of plants, but aluminum is not considered a necessary component; in fact, under some conditions there is ground for suspicion that aluminum salts are toxic. Results obtained from most of the experiments in nutrient solutions, intended to illustrate the stimulating effect of manganese, are of very doubtful value since increase in height of a plant during a short period of growth is usually the only measurement used to determine stimulation. The conclusion seems to be fairly general among most

investigators, however, that manganese in higher concentrations causes a bleaching or yellowing of the leaves and a depression in growth.

In connection directly with the manganese problem in Hawaii, Kelley (*28*, *29*, *30*, *31*, *32*), as already mentioned, had made a very thorough investigation of the manganese problem. He had established the correlation between yellowing of pineapples and an abnormal amount of manganese in the soil. The very valuable data obtained by him in his extensive series of soil and plant analyses should be consulted in conjunction with this publication as his investigations are complementary to the writer's. The toxic effects of manganese were attributed by Kelley to modification in the osmotic absorption of lime and magnesia.

At the time the writer attacked the manganese problem, the injurious effects of manganese on plants were attributed by practically all scientific investigators to an indefinite "toxic effect" and to "manganese poisoning." A large amount of literature on lime-induced chlorosis has been available for many years, and it has been known that plants on highly calcareous soils become chlorotic, and that spraying with solutions of iron sulphate overcame this chlorosis. No proof, however, had been presented to show that the indefinite "toxic effects" of manganese are in any way similar to lime-induced chlorosis, nor that manganese causes a deficiency of iron in the plant nor that spraying with solution of iron sulphate will cure "manganese poisoning." In Hawaii, pineapple plants were dying on hundreds of acres of manganese soil. No remedy having been found for this condition, except, possibly, heavy applications of stable manure, which was expensive, only temporarily beneficial, and limited in supply, many thousands of acres have been abandoned or left uncultivated. So little understood was the real nature of the manganese problem that experiments were being carried on with *coral sand* on the manganese soils. Had the "toxic effect" of manganese been known to be due to a depressed assimilation of iron by the plant, calcium carbonate, in the form of coral sand, would not have been added to depress the assimilation of iron still further.

THE MANGANIFEROUS SOILS AND THEIR EFFECT ON PINEAPPLE AND OTHER PLANTS.

COMPOSITION OF THE MANGANIFEROUS SOILS.

The chief difference in chemical composition noticed by Kelley between the black soils where "pineapple yellows" occurred, and the normal soils where the plants were healthy, was in the high content of manganese of the former. Kelley (*32*) gives the composition of these soils in the accompanying analyses.

TABLE 1.—*Composition of manganiferous and normal soils of Oahu.*

Constituents.	Manganiferous soils.									
	Soil. No. 9.	Subsoil. No. 10.	Soil. No. 11.	Subsoil. No. 12.	Soil. No. 15.	Subsoil. No. 16.	Soil. No. 27.	Subsoil. No. 28.	Soil. No. 51.	Subsoil. No. 52.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Insoluble matter	33.46	36.06	39.02	42.60	33.73	34.53	42.08	42.78	38.78	39.74
Potash (K_2O)	.83	.74	.78	.81	.99	1.07	.65	.64	.83	.76
Soda (Na_2O)	.40	.42	.36	.44	.21	.38	.32	.37	.34	.47
Lime (CaO)	1.39	.86	.64	.60	.49	.37	.19	.21	.24	.26
Magnesia (MgO)	.55	.43	.41	.39	.52	.41	.35	.28	.64	.49
Manganese oxid (Mn_3O_4)	9.74	8.76	4.80	3.50	4.01	2.43	4.14	3.59	4.32	4.24
Ferric oxid (Fe_2O_3)	19.65	21.51	18.24	20.52	26.03	26.85	22.05	21.36	20.40	25.38
Alumina (Al_2O_3)	15.50	15.74	15.40	16.89	15.82	18.98	16.01	19.51	19.35	16.14
Phosphorus pentoxid (P_2O_5)	.21	.16	.36	.13	.35	.21	.13	.11	.11	.14
Sulphur trioxid (SO_3)	.16	.09	.23	.05	.17	.05	.37	.30	.29	.28
Titanic dioxid (TiO_2)	.73	1.09	.40	.58	.85	1.58	(1)	(1)	(1)	(1)
Loss on ignition	17.73	14.45	19.71	13.72	16.68	12.83	14.02	11.31	15.29	12.45
Total	100.35	100.31	100.35	100.23	99.85	99.69	100.31	100.46	100.59	100.35
Nitrogen (N)	.39	.23	.45	.19	.35	.20	.27	-------	.24	.13

Constituents.	Normal soils.								
	Soil. No. 7.	Subsoil. No. 8.	Soil. No. 13.	Subsoil. No. 14.	Soil. No. 31.	Subsoil. No. 32.	Soil. No. 49.	Subsoil. No. 50.	Soil. No. 19.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Insoluble matter	40.89	39.25	46.52	46.37	41.73	37.16	42.36	39.82	44.00
Potash (K_2O)	.51	.60	.50	.57	.53	.57	.65	.48	.59
Soda (Na_2O)	.21	.32	.31	.13	.20	.37	.46	.20	.29
Lime (CaO)	.51	.66	.32	.31	.22	.15	.23	.12	.24
Magnesia (MgO)	.37	.38	.40	.42	.36	.30	.47	.44	.42
Manganese oxid (Mn_3O_4)	.22	.06	.33	.35	.22	.39	1.17	.36	.16
Ferric oxid (Fe_2O_3)	35.72	33.28	24.37	24.49	23.29	24.13	20.36	25.87	27.94
Alumina (Al_2O_3)	3.58	8.66	9.15	12.02	16.02	20.87	20.37	19.42	11.91
Phosphorus pentoxid (P_2O_5)	.07	.08	.09	.13	.08	.12	.10	.10	.04
Sulphur trioxid (SO_3)	.09	.07	.11	.12	.46	.33	.23	.42	.11
Titanic dioxid (TiO_2)	3.83	2.74	2.20	2.05	(1)	(1)	(1)	(1)	.28
Loss on ignition	14.22	13.99	15.98	13.17	17.22	16.38	13.22	13.33	13.95
Total	100.22	100.09	100.28	100.13	100.33	100.77	99.62	100.56	99.93
Nitrogen (N)	.34	.25	.38	.25	.29	.20	.27	.14	.29

[1] Titanium was not separated from alumina.

These analyses show that the manganiferous soils are well supplied with nitrogen, phosphoric acid, and potash, usually considered the three most important plant foods, and that they even surpass the normal soils in their supply of these constituents. Kelley showed that the black soils are superior to the average soils in physical properties, and that nitrification, one of the principal bacteriological factors affecting soil fertility, takes place more rapidly in the manganiferous soils than in the nonmanganiferous soils. Comparative solubilities in water and dilute organic acids showed little differences except in the much greater quantities of the manganese which were dissolved from the black soils.

Table 2 gives some analyses of soils on which yellowing of pineapples occurred.

TABLE 2.—*Analyses of manganiferous soils.*[1]

Constituents.	Soil laboratory numbers.						
	635	636	637	638	639	640	641
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Manganese oxid (Mn_3O_4)	0.31	4.80	5.19	5.12	2.51	5.58	2.85
Insoluble matter	29.43	39.99	38.28	39.28	39.79	38.08	39.63
Potash (K_2O)	.21	.21	.34	.33	.38	.40	.34
Soda (Na_2O)	.83	.87	.56	.62	.92	.65	.60
Lime (CaO)	.39	.39	.42	.44	.35	.43	.36
Magnesia (MgO)	.43	.61	.57	.47	.43	.40	.51
Ferric oxid (Fe_2O_3)	15.50	13.23	12.26	12.27	10.42	10.95	13.44
Alumina (Al_2O_3)	30.79	22.78	25.05	24.62	25.70	25.33	23.37
Phosphorus pentoxid (P_2O_5)	.51	.55	.51	.50	.56	.61	.53
Sulphur trioxid (SO_3)	.36	.42	.34	.32	.48	.31	.36
Volatile matter	19.76	15.63	15.71	15.50	18.06	16.89	17.23
Titanic dioxid (TiO_2)	1.74	.62	.72	.73	.73	.53	.83

[1] These soils will be referred to later in the text.

These analyses are similar to those of Kelley in that they show a high content of manganese where the yellowing occurred, with the exception of soil No. 635, which was obtained from Kunia, Oahu. The plants on this soil were yellow and produced characteristic red fruit. This soil, according to the analysis, contained only 0.31 per cent of manganese calculated as the mangano-manganic oxid. That this manganese is actually present as the dioxid will be shown, while the manganese in normal soils is probably in the silicate form.

FORM IN WHICH MANGANESE OCCURS IN THE SOIL.

Kelley, in his analyses, reported the manganese calculated as the mangano-manganic oxid (Mn_3O_4), but concluded from his investigations that at least part of the manganese is present as higher oxids, since there is a liberation of chlorin gas with acids and a change in appearance during ignition.

To determine the form in which manganese was present in the soil, the writer distilled the samples according to the Bunsen method for available oxygen in pyrolusite. Table 3 compares the manganese dioxid, calculated from these results, with the total manganese present, calculated to the same form.

TABLE 3.—*Comparison of total manganese with manganese dioxid in the manganiferous soils.*

Laboratory soil number.	Total manganese dioxid by official method.	Manganese dioxid according to the Bunsen distillation method.	Laboratory soil number.	Total manganese dioxid by official method.	Manganese dioxid according to the Bunsen distillation method.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
635	0.35	0.35	639	2.86	2.66
636	5.48	4.85	640	6.36	5.67
637	5.92	5.20	641	3.25	1.92
638	5.86	5.15			

Since the distillation method probably gives low results owing to the presence of organic matter, it is safe to conclude that nearly all the manganese present is in the form of dioxid. This assumption is

based on the fact that the usual manganese ore is the dioxid (pyrolusite), and that solutions of manganese in the carbonate form, in which form it is probable that the manganese is leached out of the original lava,[3] soon precipitate manganese dioxid because of their strong hydrolysis and oxidation by the air.

IRON IN THE MANGANIFEROUS SOILS.

Kelley (*32*) reported the presence of 18.24 to 26.85 per cent of iron as ferric oxid, while the writer found a variation of 10.42 to 15.5 per cent in the soil samples he analyzed. Hawaiian soils [4] contain an abundance of iron, having several times the quantity found in ordinary soils of the mainland or pineapple soils of other countries.

Kelley (*28*) determined the solubility of the manganese and iron with a 1 per cent solution of citric acid. In this determination he gives the average amount of iron soluble as 0.243 per cent ferric oxid, or about 8,500 pounds per acre-foot. It is a striking peculiarity that, notwithstanding the presence in these manganiferous soils of an immense quantity of total iron and of citric acid soluble iron, the pineapple plants seemed unable to assimilate the iron but showed a pronounced change after they had been sprayed with 30 to 40 pounds of iron sulphate per acre.

The failure of the plants to absorb iron, notwithstanding the large amount soluble in citric acid, seems to constitute a serious criticism of the general applicability of the citric-acid method for determining the available constituents of the soil.

REACTION OF THE MANGANIFEROUS SOILS.

The manganiferous soils when tested with litmus show an acid reaction. Kelley (*28*) examined a large number of these black soils and found most of them slightly acid and few neutral.

In order to determine more exactly the acidity of these manganese soils, the hydrogen-ion concentrations were determined electrically. The hydrogen-ion concentrations, expressed in pH values, are given in Table 4.

TABLE 4.—*Hydrogen-ion concentrations (expressed in pH values) of the manganiferous soils.*

Laboratory soil number.	Manganese oxid (Mn_3O_4).	pH value.	Laboratory soil number.	Manganese oxid (Mn_3O_4).	pH value.
	Per cent.			*Per cent.*	
9	9.74	6.5	636	4.80	6.1
11	4.80	6.4	638	5.12	6.3
15	4.01	7.0	639	2.51	6.0
27	4.14	5.7	641	2.85	6.0
51	4.32	5.9			

The table indicates that the manganese soils in nearly every instance are fairly acid, since soils having a pH value lower than 7, the neutral point of pure water, are acid. That these soils are lacking in carbonate of lime is proved by the fact that calcareous soils would have

[3] Lava is the original material from which nearly all the upland soils of the island are derived.
[4] Iron is one of the most abundant elements of Hawaiian soils.

an alkaline reaction and a pH value approximately 8.2–8.4 (that of carbonate of lime in water).

AMOUNT AND FORM OF LIME IN THE MANGANIFEROUS SOILS.[6]

The amount of lime that is contained in manganiferous soils is of interest in connection with the reaction of these soils. Kelley reported manganiferous soils containing as low as 0.19 and 0.24 per cent of lime, and his figures average about 0.05 per cent of lime. (See Table 1.) Soils analyzed by the writer averaged about 0.4 per cent of lime. (See Table 2.)

An attempt was made to determine the presence of carbonates in the manganiferous soils by the methods of MacIntire and Willis (*34*, *35*) of treating the soils with 1–15 H_3PO_4, and by their later method with 1–15 HCl. Table 5 gives the results.

TABLE 5.—*Carbon dioxid content of the manganiferous soils by the method of MacIntire and Willis.*

Laboratory soil number.	Carbon dioxid (1/15 H_3PO_4).	Carbon dioxid (1/15 HCl).	Laboratory soil number.	Carbon dioxid (1/15 H_3PO_4).	Carbon dioxid (1/15 HCl).
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
635	0.03	0.04	639	0.04	0.03
636	.04	.07	640	.03	.05
637	.02	.06	641	.03	.06
638	.03	.06			

The quantity of carbon dioxid found in these soils was negligible and indicated the practical absence of carbonates, as soils that are known to be free from carbon dioxid produce considerable amounts of CO_2 owing to the action of acids on the soil organic matter. The values which were found for the hydrogen-ion concentrations of these soils proved the absence from them of calcium carbonate. The small quantity of lime in the soils is, therefore, probably present in the form of silicate and not as carbonate. Some of it may be present as a manganite, as James (*23*) suggests. It will be shown later that the injurious effects of the manganiferous soils are due to deficiencies of iron in the plant and not to toxic effects of calcium manganite, as James further suggests.

EFFECTS OF MANGANESE ON RICE.

It has already been explained that the toxic effects of manganiferous soils on pineapple plants are characterized by yellowing of the leaves, cracking open and decaying of immature fruit, which is stunted and red or pink instead of normal size and green, and by a general unhealthy appearance of the plants. The injurious effects of manganese are very completely described by Wilcox and Kelley (*46*) and by Kelley (*28*, *29*, *30*, *31*, *32*).

[6] Constituents other than lime do not appear of significance since they show little variation from the normal.

Growth of Rice in Nutrient Solutions.

In order to investigate the influence of manganese more fully and without the complication of soil phenomena, various experiments were conducted in nutrient solutions with the addition of manganese sulphate and manganese dioxid. Rice, which is similar to the pineapple in its susceptibility to chlorosis, was used in these experiments because it is more convenient of culture in nutrient solutions and furnishes results more quickly than the pineapple plant.

Experiment I.—This experiment was divided into two series of nine tests each, using the nutrient solutions shown in Table 6.

Table 6.—*Nutrient solutions used.*

Series I.—Loew and Sawa's (*33*) nutrient solution.	Quantity.	Series II.—Gile and Carrero's (*17*) acid nutrient solution.	Weight.
	Per cent.		*Grams.*
Calcium nitrate	0.04	Potassium nitrate	0.1017
Magnesium sulphate	.01	Monobasic potassium phosphate	.0714
Potassium nitrate	.03	Sodium nitrate	.2143
Monopotassium phosphate	.02	Sodium sulphate	.0315
Ammonium sulphate	.01	Calcium chlorid	.05
Ferrous sulphate	.01	Magnesium chlorid	.05
		Ferric chlorid	.0041
		Sulphuric acid c.c. N/m	.5
		Distilled water c.c.	1.000

The manganese dioxid used in all the experiments was prepared by Merck and marked "artificial," and "pure," and contained about 90 per cent MnO_2. Ten grams of this manganese dioxid in 200 cubic centimeters of pure water gave, on 18 and 42 hours' contact, a pH value of about 6.6, or a faintly acid reaction. Coral sand and calcium carbonate under the same conditions gave a pH value of about 8.4 or a distinctly alkaline reaction.

Rice seedlings were germinated in distilled water and transferred to the various nutrient solutions when the plumules were about 2 inches long. Four plants each were grown in large flasks. Duplicate tests of each trial were made. Transpired water was replaced with distilled water daily and the solutions were changed every fourth day. The solutions were freshly made 18 hours before changing and the flasks and roots were rinsed with a little of the fresh solution when the changes were made. The plants were grown for 40 days.

The plants were harvested on the fortieth day and the green and dry weights of the stalks and leaves and of the roots were determined. The results are given in Tables 7 and 8.

TABLE 7.—*Weight and condition of rice grown in Loew and Sawa's nutrient solution to which manganous sulphate, manganese dioxid, and calcium carbonate were added.*

Series.	Culture solutions with amount of added material per liter.	Flask No.	Green weight of stalks and leaves.	Oven-dry weight of stalks and leaves.	Oven-dry weight of roots.	Average oven-dry weight.		Condition of plant
						Stalks and leaves.	Whole plant.	
			Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	
A	Check; sol.+0.037 gm. Fe from $FeSO_4$.	1	2.86	0.58	0.17			Green; healthy.
		2	3.70	.66	.21	0.62	0.81	
B	Sol.+0.037 gm. Fe from $FeSO_4$+0.072 gm. Mn from $MnSO_4$.	3	2.35	.48	.14			Green; older leaves spotted with brown.
		4	2.29	.48	.15	.48	.63	
C	Sol.+0.072 gm. Mn from $MnSO_4$; Fe omitted.	5	.10	.04	.03			Dead.
		6	.15	.05	.04	.05	.08	
D	Sol.+0.037 gm. Fe from $FeSO_4$+0.036 gm. Mn from $MnSO_4$.	7	3.04	.58	.18			Green; older leaves spotted with brown.
		8	3.59	.59	.19	.59	.77	
E	Sol.+0.037 gm. Fe from $FeSO_4$+0.018 gm. Mn from $MnSO_4$.	9	2.66	.46	.28			Green; healthy.
		10	2.67	.61	.14	.54	.75	
F	Sol.+0.037 gm. Fe from $FeSO_4$+0.004 gm. Mn from $MnSO_4$.	11	3.44	.59	.22			Do.
		12	4.15	.76	.25	.67	.80	
G	Sol.+0.037 gm. Fe from $FeSO_4$+0.4 gm. MnO_2.	13	4.63	.86	.26			Do.
		14	4.60	.82	.22	.84	1.08	
H	Sol.+0.037 gm. Fe from $FeSO_4$+0.4 gm. MnO^2 +0.4 gm. $CaCO_3$.	15	4.59	.79	.24			Do.
		16	4.58	.67	.23	.73	.96	
I	Sol.+0.037 gm. Fe from $FeSO_4$+0.4 gm. $CaCO_3$.	17	5.42	.89	.43			Do.
		18	6.74	1.06	.51	.98	1.45	

TABLE 8.—*Weight and condition of rice grown in Gile and Carrero's nutrient solution to which manganous sulphate, manganese dioxid, and calcium carbonate were added.*

Series.	Culture solutions with amount of added material per liter.	Flask No.	Green weight of stalks and leaves.	Oven-dry weight of stalks and leaves.	Oven-dry weight of roots.	Average oven-dry weight.		Condition of plant
						Stalks and leaves.	Whole plant.	
			Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	
J	Check; sol.+0.0014 gm. Fe from $FeCl_3$.	19	3.01	0.52	0.23			Green; healthy.
		20	2.71	.46	.19	0.49	0.70	
K	Sol.+0.0014 gm. Fe from $FeCl_3$+0.072 gm. Mn from $MnSO_4$.	21	.20	.07	.04			Leaves shriveled; brown; nearly dead.
		22	.25	.07	.04	.07	.11	
L	Sol.+0.072 gm. Mn from $MnSO_4$; Fe omitted.	23	.13	.04	.04			Dead.
		24	.07	.03	.04	.04	.08	
M	Sol.+0.0014 gm. Fe from $FeCl_3$+0.036 gm. Mn from $MnSO_4$.	25	.65	.14	.05			Leaves brown spotted with dark brown.
		26	.72	.16	.07	.15	.21	
N	Sol.+0.0014 gm. Fe from $FeCl_3$+0.018 gm. Mn from $MnSO_4$.	27	1.11	.21	.07			Leaves yellow and brownish.
		28	.58	.12	.04	.17	.22	
O	Sol.+0.0014 gm. Fe from $FeCl_3$+0.004 gm. Mn from $MnSO_4$.	29	2.16	.40	.13			Lower leaves spotted with brown.
		30	1.08	.21	.08	.31	.42	
P	Sol.+0.0014 gm. Fe from $FeCl_3$+0.4 gm. MnO_2.	31	.05	.03	.04			Nearly dead; light brownish white color.
		32	.07	.04	.04	.04	.08	
Q	Sol.+0.0014 gm. Fe from $FeCl_3$+0.4 gm. Mn from $MnSO_4$+0.4 gm. $CaCO_3$.	33	.08	.05	.04			Bleached; yellowish-white; stunted.
		34	.08	.05	.05	.05	.10	
R	Sol.+0.0014 gm. Fe from $FeCl_3$+0.4 gm. $CaCO_3$.	35	.09	.05	.04			Do.
		36	.09	.05	.05	.05	.10	

With Loew and Sawa's nutrient solution, manganous sulphate did not cause chlorosis but a decrease in the dry weights of the plants, except in the smallest amount used. On the other hand, manganese dioxid and calcium carbonate, singly and in combination, caused a tremendous increase in the growth of the plants. Evidently, then, this solution contained an excessive amount of iron, and the increase in growth was due to manganese dioxid and calcium carbonate depressing the assimilation of some of this harmful iron. This nutrient solution is the one with which Loew and Sawa obtained results which they claimed proved the supposedly stimulating effect of manganese. The stimulating effect of manganese in this nutrient solution is doubtless due to its depressing effect on the assimilation of the excessive amounts of iron in the solution.

With Gile and Carrero's acid nutrient solution, an amount as small as 4 milligrams per liter of manganese from manganous sulphate (0.001 per cent of manganous sulphate) was sufficient to cause brown spotting of the leaves and a decided decrease in rate of growth. Practically no growth was made in the presence of manganese dioxid or calcium carbonate and the plants were strongly chlorotic. The greatly different effects of manganese in these two nutrient solutions seemed to be due either to the form or to the amounts of iron supplied. A second experiment was therefore undertaken in which different forms of iron were used in the same solution.

Experiment II.—In order to obtain results comparable with those recorded by Gile and Carrero (*18*), it was decided to use their neutral nutrient solution in all the later experiments. This solution had the composition shown in Table 9.

TABLE 9.—*Gile and Carrero's neutral nutrient solution.*

Composition.	Weight.	Composition.	Weight.
	Grams.		*Grams.*
Potassium nitrate	10.71	Sodium sulphate	3.15
Monobasic potassium phosphate	3.57	Calcium chlorid	2.00
Dibasic potassium phosphate	3.57	Magnesium chlorid	2.00
Sodium nitrate	21.43	Distilled water	100,000

This experiment was similar to Experiment I. Twelve tests were made.

On the fortieth day the plants were harvested and the weights determined. The results are given in Table 10.

TABLE 10.—*Comparative weights of rice plants which were grown in nutrient solutions containing manganous sulphate and manganese dioxid solutions, to which iron as ferrous sulphate, ferric chlorid, and ferric citrate was added.*

Series.	Culture solutions with amount of added material per liter.	Flask No.	Green weight of stalks and leaves.	Oven-dry weight of stalks and leaves.	Oven-dry weight of roots.	Average oven-dry weight.		Condition of plants.
						Stalks and leaves.	Whole plant.	
			Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	
A_1	Check; sol.+0.008 gm. Fe from $FeSO_4$.	1	5.77	1.04	0.39			Green; healthy.
		2	6.01	1.03	.37	1.04	1.42	
A_2	Sol.+0.008 gm. Fe from $FeSO_4$+0.072 gm. Mn from $MnSO_4$.	3	.80	.20	.07			Stunted; light-colored, spotted with brown.
		4	.72	.20	.06	.20	.27	
A_3	Sol.+0.008 gm. Fe from $FeSO_4$+0.007 gm. Mn from $MnSO_4$.	5	3.18	.65	.22			Somewhat stunted; light-colored.
		6	2.38	.56	.19	.61	.81	
A_4	Sol.+0.008 gm. Fe from $FeSO_4$+0.4 gm. MnO_2.	7	.28	.07	.04			Very stunted; yellow and bleached; spotted with brown.
		8	.28	.06	.05	.07	.11	
B_1	Sol.+0.008 gm. Fe from $FeCl_3$.	9	5.04	.87	.31			Green; healthy.
		10	4.66	.85	.25	.86	1.14	
B_2	Sol.+0.008 gm. Fe from $FeCl_3$+0.072 gm. $MnSO_4$.	11	.23	.05	.04			Extremely stunted; leaves withered; practically dead.
		12	.27	.10	.04	.08	.12	
B_3	Sol.+0.008 gm. Fe from $FeCl_3$+0.007 gm. $MnSO_4$.	13	1.91	.46	.15			Stunted; light-colored.
		14	1.42	.38	.14	.42	.57	
B_4	Sol.+0.008 gm. Fe from $FeCl_3$+0.4 gm. MnO_2.	15	.15	.04	.04			Very stunted; leaves almost white.
		16	.20	.06	.04	.05	.09	
C_1	Sol.+0.008 gm. Fe from $Fe_2(C_6H_5O_7)_2$.	17	3.40	.56	.20			Green; healthy.
		18	4.94	.79	.31	.68	.93	
C_2	Sol.+0.008 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.072 gm. Mn from $MnSO_4$.	19	.11	.04	.04			Withered and dead.
		20	.08	.03	.04	.04	.08	
C_3	Sol.+0.008 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.007 gm. Mn from $MnSO_4$.	21	.25	.06	.04			Very pale greenish-yellow; leaves withered.
		22	.29	.06	.04	.06	.10	
C_4	Sol.+0.008 gm. $Fe_2(C_6H_5O_7)_2$ +0.4 gm. MnO_2.	23	.49	.10	.06			Leaves yellow, spotted with brown.
		24	.49	.12	.05	.11	.17	

The form in which iron was supplied did not seem to change the effects of the manganese. As small an amount as 7 milligrams per liter of manganese as manganous sulphate (0.002 per cent of manganous sulphate) caused chlorosis and a very striking decrease in weight of plants. Manganese dioxid produced a similar effect. Ferrous sulphate appeared to be the best source of iron supply, with ferric chlorid next, and ferric citrate last.

Experiment III.—It was decided to investigate more thoroughly the effects of varying amounts of iron, because the effects of manganese seemed to depend largely on the iron content in the nutrient solution. Tests with nutrient solution which had been used in Experiment II were repeated. Two plants were grown in each flask, two flasks were taken as a unit, and the units were triplicated for each variable. Eighteen tests were made.

The leaves of the plants in series A_4, B_4, and C_4 were dipped in a 0.5 per cent solution of ferrous sulphate several hours before the nutrient solutions were changed so as to minimize chances of the dipping solution getting into the nutrient solution.

Representative plants of each trial were photographed on the fortieth day just before harvesting. The weights of the harvested plants are given in Table 11 and graphically in Figure 1.

TABLE 11.—*Comparative weights of rice plants which were grown in manganous sulphate and manganese dioxid solutions to which were added various amounts of iron as ferrous sulphate.*

Series.	Culture solutions with amount of added material per liter.	Flask No.	Green weight of stalks and leaves.	Oven-dry weight of stalks and leaves.	Oven-dry weight of roots.	Average oven-dry weight.		Condition of plants.
						Stalks and leaves.	Whole plant.	
			Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	
A_1	Sol.+0.005 gm. Fe from $FeSo_4$.	1-2	15.05	2.41	1.05	------	-------	Fine; green.
		3-4	15.48	2.53	1.07	------	-------	
		5-6	15.71	2.48	1.00	2.4	3.51	
A_2	Sol.+0.005 gm. Fe from $FeSO_4$+0.4 gm. MnO_2.	7-8	.29	.08	.06	-------	-------	Leaves white, spotted with brown; shriveled and stunted; dead.
		9-10	.29	.07	.06	-------	-------	
		11-12	.32	.08	.06	.08	.14	
A_3	Sol.+0.005 gm. Fe from $FeSO_4$+0.018 gm. Mn from $MnSO_4$.	13-14	.67	.16	.06	-------	-------	Light yellowish-green, spotted with brown; older leaves very chlorotic, shriveled, and stunted.
		15-16	.62	.14	.06	-------	-------	
		17-18	.64	.15	.06	.15	.21	
A_4	Sol.+0.005 gm. Fe from $FeSO_4$+0.4 gm. MnO_2; leaves dipped in 0.5 per cent $FeSO_4$ solution.	19-20	2.15	.43	.17	-------	-------	Great improvement over A_2; light green; spotted with dark green where iron penetrated; few brown spots on leaves.
		21-22	2.15	.42	.22	-------	-------	
		23-24	2.17	.44	.18	.43	.62	
B_1	Sol.+0.010 gm. Fe from $FeSO_4$.	25-26	15.21	2.56	1.06	-------	-------	Fine; green.
		27-28	15.17	2.56	1.07	-------	-------	
		29-30	15.47	2.65	1.01	2.59	3.64	
B_2	Sol.+0.010 gm. Fe from $FeSO_4$+0.400 gm. MnO_2.	31-32	.32	.10	.06	-------	-------	Bleached; spotted with brown; slightly better than A_2.
		33-34	.35	.10	.07	-------	-------	
		35-36	.27	.09	.05	.10	.16	
B_3	Sol.+0.010 gm. Fe from $FeSO_4$+0.018 gm. Mn from $MnSO_4$.	37-38	5.91	1.28	.39	-------	-------	Light green spotted with brown; still stunted.
		39-40	5.95	1.33	.41	-------	-------	
		41-42	6.13	1.29	.40	1.30	1.70	
B_4	Sol.+0.010 gm. Fe from $FeSO_4$+0.4 gm. MnO_2; leaves dipped in 0.5 per cent $FeSO_4$ solution.	43-44	1.55	.37	.13	-------	-------	About same as A_4; decided improvement over B_2.
		45-46	1.50	.37	.12	-------	-------	
		47-48	1.67	.40	.16	.38	.52	
C_1	Sol.+0.020 gm. Fe from $FeSO_4$.	49-50	13.69	2.26	.90	-------	-------	Fine; green.
		51-52	13.64	2.21	.81	-------	-------	
		53-54	14.87	2.51	.99	2.33	3.23	
C_2	Sol.+0.020 gm. Fe from $FeSO_4$+0.4 gm. MnO_2.	55-56	2.25	.50	.16	-------	-------	Somewhat stunted; light green spotted with some brown.
		57-58	2.76	.60	.19	-------	-------	
		59-60	2.51	.56	.18	.55	.73	
C_3	Sol.+0.020 gm. Fe from $FeSO_4$+0.018 gm. Mn from $MnSO_4$.	61-62	6.93	1.43	.41	-------	-------	Dark green; inferior in size to C_1; older leaves shriveled, but showed scarcely a trace of brown.
		63-64	7.15	1.48	.48	-------	-------	
		65-66	6.61	1.40	.47	1.44	1.89	
C_4	Sol.+0.020 gm. Fe from $FeSO_4$+0.4 gm. MnO_2; leaves dipped in 0.5 per cent $FeSO_4$ solution.	67-68	2.48	.58	.20	-------	-------	About same as B_4; dark green spots where iron penetrated.
		69-70	2.63	.62	.23	-------	-------	
		71-72	2.66	.62	.26	.61	.84	
D_1	Sol.+0.040 gm. Fe from $FeSO_4$.	73-74	13.56	2.41	.76	-------	-------	Dark green.
		75-76	12.78	2.17	.79	-------	-------	
		77-78	13.24	2.30	.85	2.29	3.09	
D_2	Sol.+0.040 gm. Fe from $FeSO_4$+0.4 gm. MnO_2.	79-80	12.44	2.33	.74	-------	-------	Do.
		81-82	12.45	2.30	.71	-------	-------	
		83-84	12.23	2.30	.76	2.31	3.04	
D_3	Sol.+0.040 gm. Fe from $FeSO_4$+0.018 gm. Mn from $MnSO_4$.	85-86	11.70	1.95	.68	-------	-------	Do.
		87-88	12.06	2.03	.70	-------	-------	
		89-90	12.05	2.06	.71	2.01	2.71	
E_1	Sol.+0.080 gm. Fe from $FeSO_4$.	91-92	7.89	1.51	.64	-------	-------	Do.
		93-94	7.94	1.48	.58	-------	-------	
		95-96	7.28	1.41	.61	1.47	2.08	
E_2	Sol.+0.080 gm. Fe from $FeSO_4$+0.4 gm. MnO_2.	97-98	9.78	1.73	.85	-------	-------	Do.
		99-100	9.44	1.69	.86	-------	-------	
		101-102	9.77	1.73	.84	1.72	2.57	
E_3	Sol.+0.080 gm. Fe from $FeSO_4$+0.018 gm. Mn from $MnSO_4$.	103-104	6.99	1.38	.59	-------	-------	Do.
		105-106	7.59	1.42	.62	-------	-------	
		107-108	7.05	1.40	.62	1.40	2.01	

The text to Figure 1 and Table 11 show that chlorosis and severe depression in growth were caused by manganese dioxid, with 5, 10, or 20 milligrams per liter of iron supplied from ferrous sulphate, and also by 18 milligrams per liter of manganese from manganous sulphate (0.005 per cent manganous sulphate). When the leaves were dipped in iron solution chlorosis was overcome, but full normal growth was

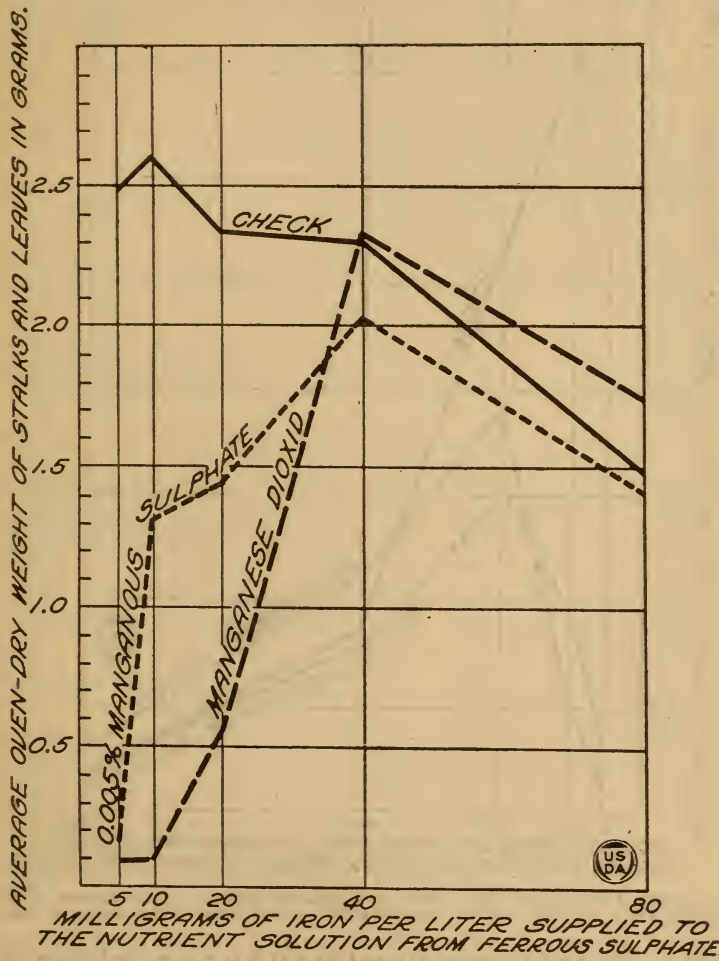

FIG. 1.—(Results of Experiment III.) Effect of manganous sulphate and manganese dioxid on the growth of rice in nutrient solutions with various amounts of iron supplied from ferrous sulphate.

not induced. The writer found it very difficult to supply iron to the leaves of the rice plant because they seem adapted for shedding solutions. Where the iron penetrated the leaves, very dark green spots appeared. When the amount of iron in the solution was increased excessively, the chlorotic effect of manganese was completely overcome. In fact, apparently, because of its removal of some of the excessive iron, manganese dioxid gave slightly better results than the check.

Experiment IV.—Experiment III was repeated, using a different form of iron. The different variables were the same as in Experiment III except that ferric chlorid was the source of iron, and the plants

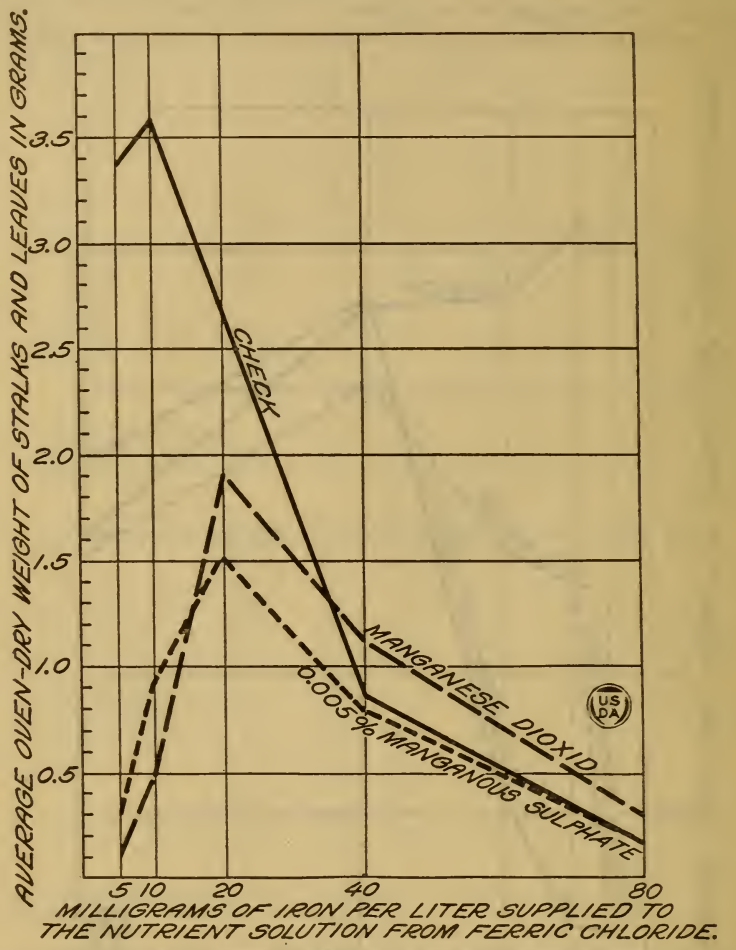

FIG. 2.—(Results of Experiment IV.) Effect of manganous sulphate and manganese dioxid on the growth of rice in nutrient solutions supplied with various amounts of iron from ferric chlorid.

in series A_4, B_4, and C_4 were dipped in a 0.5 per cent solution of ferric chlorid instead of ferrous sulphate.

The weights of the plants on the fortieth day are given in Table 12 and graphically in Figure 2.

TABLE 12.—*Comparative weights of rice plants which were grown in manganous sulphate and manganese dioxid solutions to which were added various amounts of iron as ferric chlorid.*

Series.	Culture solutions with amount of added material per liter.	Flask No.	Green weight of stalks and leaves.	Oven-dry weight of stalks and leaves.	Oven-dry weight of roots.	Average oven-dry weight.		Condition of plants.
						Stalks and leaves.	Whole plant.	
			Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	
A_1	Sol.+0.005 gm. Fe from $FeCl_3$	1–2	20.50	3.33	1.30			Very fine; green; healthy.
		3–4	20.34	3.39	1.34			
		5–6	19.89	3.33	1.30	3.35	4.66	
A_2	Sol.+0.005 gm. Fe from $FeCl_3$+0.4 gm. MnO_2.	7–8	.25	.09	.06			Bleached white; withered; very stunted; practically dead.
		9–10	.28	.09	.06			
		11–12	.28	.09	.06	.09	.15	
A_3	Sol.+0.005 gm. Fe from $FeCl_3$+0.018 gm. Mn from $MnSO_4$.	13–14	1.15	.30	.08			Very stunted; yellowish; lower leaves withered and spotted with brown.
		15–16	1.14	.30	.08			
		17–18	1.16	.31	.08	.30	.38	
A_4	Sol.+0.005 gm. Fe from $FeCl_3$+0.4 gm. MnO_4; leaves dipped in 0.5 per cent $FeCl_3$ solution.	19–20	.85	.24	.11			Decided improvement over A_2; yellowish-green, showing dark green spots where iron penetrated.
		21–22	.93	.25	.11			
		23–24	.92	.23	.10	.24	.35	
B_1	Sol.+0.010 gm. Fe from $FeCl_3$.	25–26	20.52	3.64	1.34			Green; healthy.
		27–28	20.48	3.60	1.23			
		29–30	19.97	3.46	1.16	3.57	4.81	
B_2	Sol.+0.010 gm. Fe from $FeCl_3$+0.4 gm. MnO_2.	31–32	2.37	.50	.16			Stunted; yellowish-green spotted with brown.
		33–34	1.87	.43	.14			
		35–36	2.16	.48	.18	.47	.63	
B_3	Sol.+0.010 gm. Fe from $FeCl_3$+0.018 gm. Mn from $MnSO_4$.	37–38	3.92	.92	.20			Light green; lower leaves withered.
		39–40	3.79	.91	.17			
		41–42	4.13	.95	.21	.93	1.12	
B_4	Sol.+0.010 gm. Fe from $FeCl_3$; leaves dipped in 0.5 per cent $FeCl_3$ solution.	43–44	5.84	1.16	.45			Decided improvement over B_2; light-green spotted with dark green where iron penetrated.
		45–46	5.73	1.13	.46			
		47–48	5.68	1.11	.44	1.13	1.58	
C_1	Sol.+0.020 gm. Fe from $FeCl_3$.	49–50	15.58	2.60	.78			Green; healthy.
		51–52	16.83	2.89	.94			
		53–54	15.38	2.61	.78	2.70	3.53	
C_2	Sol.+0.020 gm. Fe from 0.4 gm. MnO_2.	55–56	10.72	1.83	.61			Leaves rather light green, showing only few brown spots.
		57–58	10.70	1.87	.65			
		59–60	1.17	2.00	.67	1.90	2.54	
C_3	Sol.+0.020 gm. Fe from $FeCl_3$+0.018 gm. Mn from $MnSO_4$.	61–62	6.56	1.56	.38			Few brown spots on lower leaves.
		63–64	7.16	1.53	.36			
		65–66	6.26	1.43	.38	1.51	1.88	
C_4	Sol.+0.020 gm. Fe from $FeCl_3$; leaves dipped in 0.5 per cent $FeCl_3$ solution.	67–68	9.58	1.83	.67			About same as C_2.
		69–70	10.15	1.91	.74			
		71–72	10.70	1.86	.77	1.87	2.60	
D_1	Sol.+0.040 gm. Fe from $FeCl_3$.	73–74	3.17	.82	.35			Much smaller than A_1; dark green; roots formed fuzzy ball but apparently were unable to enter the solution.
		75–76	3.58	.91	.34			
		77–78	3.06	.78	.29	.84	1.17	
D_2	Sol.+0.040 gm. Fe from $FeCl_3$+0.4 gm. MnO_2.	79–80	4.58	1.09	.46			Slightly larger than D_1; dark green.
		81–82	4.96	1.18	.38			
		83–84	4.70	1.12	.42	1.13	1.55	
D_3	Sol.+0.040 gm. Fe from $FeCl_3$+0.018 gm. Mn from $MnSO_4$.	85–86	2.98	.75	.29			Dark green.
		87–88	2.85	.67	.27			
		89–90	2.96	.72	.28	.71	.99	
E_1	Sol.+0.080 gm. Fe from $FeCl_3$.	91–92	.42	.14	.08			Very stunted; leaves withered; only a few struggling roots with brown iron deposit.
		93–94	.67	.20	.10			
		95–96	.42	.12	.07	.15	.23	
E_2	Sol.+0.080 gm. Fe from $FeCl_3$+0.4 gm. MnO_2.	97–98	1.16	.30	.09			Larger than E_1 with better roots.
		99–100	1.18	.31	.09			
		101–102	1.30	.36	.12	.32	.42	
E_3	Sol.+0.080 gm. Fe from $FeCl_3$+0.018 gm. Mn from $MnSO_4$.	103–104	.66	.19	.11			About same as E_1.
		105–106	.64	.18	.12			
		107–108	.59	.17	.11	.18	.29	

The results of Experiment IV are similar to those of Experiment III. Manganese dioxid with 5, 10, or 20 milligrams per liter of iron supplied as ferric chlorid and 18 milligrams per liter of manganese as manganous sulphate (0.005 per cent manganous sulphate) caused chlorosis and a severe depression in growth. When the leaves were dipped in iron solution the chlorosis was largely overcome but normal growth was not fully induced. Very dark green spots formed on the dipped leaves where the iron penetrated. The chlorotic effects of

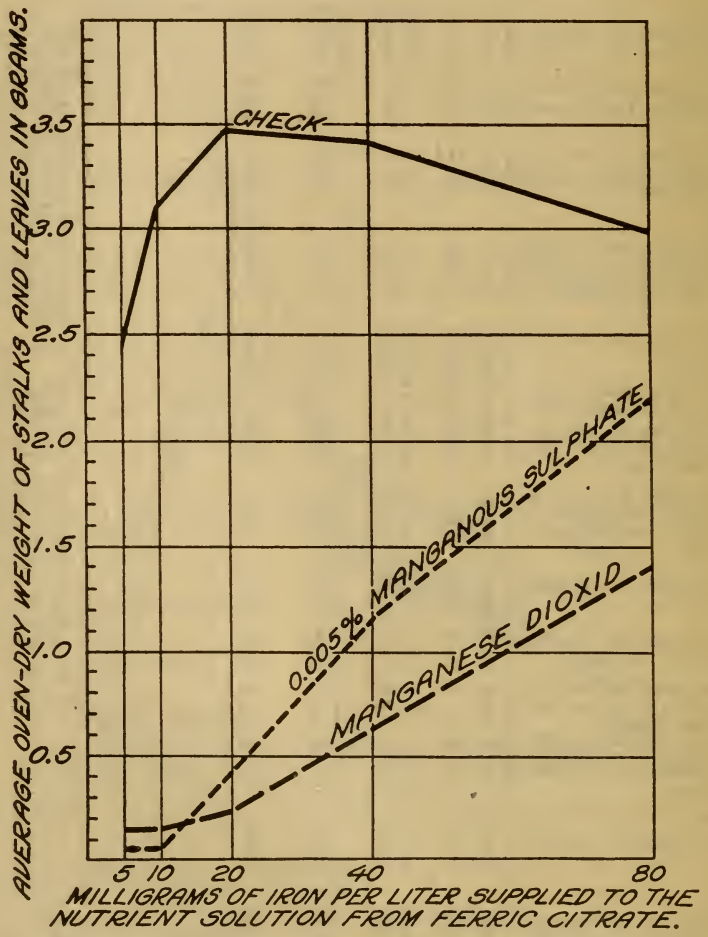

FIG. 3.—(Results of Experiment V.) Effect of manganous sulphate and maganese dioxid on the growth of rice in nutrient solutions supplied with various amounts of iron from ferric citrate.

manganese were completely overcome when the amount of iron in the solution was increased to 40 and 80 milligrams per liter, but the checks were injured by this amount of iron from ferric chlorid. Manganese dioxid, by its removal of some of this excessive iron, gave slightly better results than the check.

Experiment V.—This was a repetition of Experiment III. The different variables were the same as in Experiment III except that

ferric citrate was substituted for ferrous sulphate as the source of iron and the plants in series A_4, B_4, and C_4 were dipped in a 0.5 per cent solution of ferric citrate instead of ferrous sulphate.

The weights of the plants on the fortieth day are given in Table 13 and graphically in Figure 3.

TABLE 13.—*Comparative weights of rice plants which were grown in manganous sulphate and manganese dioxid solutions to which were added various amounts of iron as ferric citrate.*

Series.	Culture solution with amount of added material per liter.	Flask No.	Green weight of stalks and leaves.	Oven-dry weight of stalks and leaves.	Oven-dry weight of roots.	Average oven-dry weight.		Condition of plants.
						Stalks and leaves.	Whole plant.	
			Grams.	*Grams.*	*Grams*	*Grams.*	*Grams.*	
A_1	Sol.+0.005 gm. Fe from $Fe_2(C_6H_5O_7)_2$.	1–2	15.61	2.41	1.00			Fine, green plants.
		3–4	14.16	2.29	.85			
		5–6	15.98	2.56	1.06	2.42	3.39	
A_2	Sol.+0.005 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2.	7–8	.59	.11	.08			Very stunted; yellowish-white spotted with brown.
		9–10	.85	.18	.11			
		11–12	.61	.13	.07	.14	.23	
A_3	Sol.+0.005 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.018 gm. Mn from $MnSO_4$.	13–14	.16	.07	.04			Withered; brown; practically dead.
		15–16	.15	.07	.04			
		17–18	.16	.07	.04	.07	.11	
A_4	Sol.+0.005 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2; leaves dipped in a 0.5 per cent $Fe_2(C_6H_5O_7)_2$ solution.	19–20	1.60	.32	.19			Decided improvement over A_3; light green spotted with dark green where iron penetrated.
		21–22	1.62	.25	.14			
		23–24	1.20	.30	.17	.29	.46	
B_1	Sol.+0.010 gm. Fe from $Fe_2(C_6H_5O_7)_2$.	25–26	16.85	2.99	1.00			Fine, dark green plants.
		27–28	17.44	3.06	1.04			
		29–30	17.14	3.19	1.10	3.08	4.13	
B_2	Sol.+0.010 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2.	31–32	.63	.14	.08			Same as A_2; leaves bleached.
		33–34	.53	.13	.07			
		35–36	.55	.13	.07	.13	.20	
B_3	Sol.+0.010 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.018 gm. Mn from $MnSO_4$.	37–38	.12	.05	.04			Same as A_3.
		39–40	.13	.06	.04			
		41–42	.17	.06	.05	.06	.10	
B_4	Sol.+0.010 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2; leaves dipped in a 0.5 per cent $Fe_2(C_6H_5O_7)_2$ solution.	43–44	.97	.23	.10			Decided improvement over B_3; light green spotted with dark green where iron penetrated.
		45–46	1.05	.24	.09			
		47–48	.91	.21	.13	.23	.34	
C_1	Sol.+0.020 gm. Fe from $Fe_2(C_6H_5O_7)_2$.	49–50	18.33	3.43	1.17			Fine, green plants.
		51–52	18.47	3.34	.95			
		53–54	18.39	3.52	1.08	3.43	4.50	
C_2	Sol.+0.020 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2.	55–56	.79	.20	.11			Yellowish-white; stunted; spotted with brown.
		57–58	.95	.23	.11			
		59–60	1.09	.26	.12	.23	.34	
C_3	Sol.+0.020 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.018 gm. Mn from $MnSO_4$.	61–62	1.68	.42	.18			About same as C_2.
		63–64	1.59	.41	.17			
		65–66	1.44	.35	.14	.39	.55	
C_4	Sol.+0.020 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2; leaves dipped in a 0.5 per cent $Fe_2(C_6H_5O_7)_2$ solution.	67–68	3.40	.73	.37			Good, dark green, spotted with very little brown.
		69–70	3.22	.74	.37			
		71–72	3.88	.74	.37	.74	1.11	
D_1	Sol.+0.040 gm. Fe from $Fe_2(C_6H_5O_7)_2$.	73–74	17.90	3.07	1.22			Fine, green plants.
		75–76	18.96	3.40	1.31			
		77–78	19.40	3.66	1.10	3.38	4.59	
D_2	Sol.+0.040 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2.	79–80	5.27	1.04	.56			Light green; good plants spotted with little brown
		81–82	6.79	1.25	.64			
		83–84	5.67	1.08	.59	1.12	1.72	
D_3	Sol.+0.040 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.018 gm. Mn from $MnSO_4$.	85–86	9.01	1.81	.59			Same as D_2.
		87–88	9.44	1.95	.61			
		89–90	8.78	1.82	.65	1.86	2.48	
E_1	Sol.+0.080 gm. Fe from $Fe_2(C_6H_5O_7)_2$.	91–92	15.27	2.95	1.45			Fine, green plants.
		93–94	16.06	2.86	1.53			
		95–96	16.57	3.03	1.69	2.95	4.51	
E_2	Sol.+0.080 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.4 gm. MnO_2.	97–98	6.47	1.34	.65			Light green; very few brown spots; fairly good plants.
		99–100	6.53	1.36	.67			
		101–102	6.68	1.41	.60	1.37	2.01	
E_3	Sol.+0.080 gm. Fe from $Fe_2(C_6H_5O_7)_2$+0.018 gm. Mn from $MnSO_4$.	103–104	9.84	2.21	1.01			Light green; no brown spots; fairly good plants.
		105–106	9.80	2.08	.92			
		107–108	9.78	2.18	.98	2.16	3.13	

Manganese dioxid with 5, 10, and 20 milligrams of iron per liter from ferric citrate and 18 milligrams per liter of manganese from manganous sulphate (0.005 per cent manganous sulphate) caused a strong chlorosis and a severe depression in growth. Chlorosis was overcome and growth increased as a result of dipping the leaves in solutions of ferric citrate. The chlorotic effect of manganese was overcome and the weights approached those of the checks when the supply of iron in the solution was increased to 40 and 80 milli-

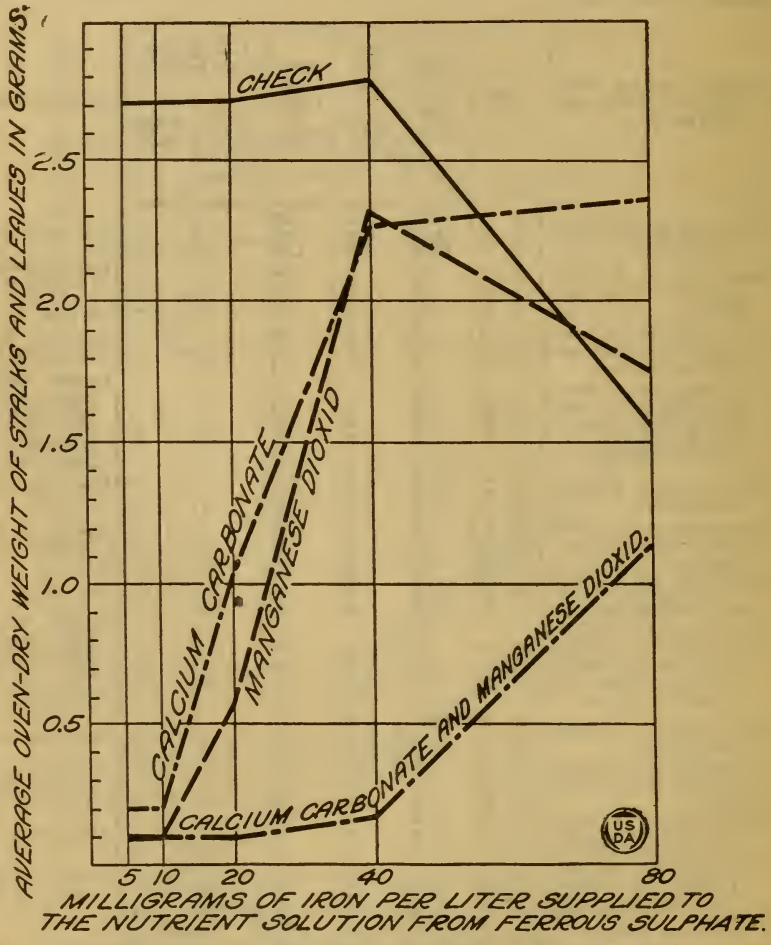

FIG. 4.—(Results of Experiment VI.) Effect of calcium carbonate and manganese dioxid on the growth of rice in nutrient solutions supplied with various amounts of iron from ferrous sulphate.

grams. Here, where there were no harmful effects due to the presence of excessive iron in the solutions, increased growth was not made, because of the presence of manganese dioxid.

Experiment VI.—Since the action of manganese in causing chlorosis is similar to that of calcium carbonate, this experiment was made to determine the effects of the latter.

The weights of the plants on the fortieth day are given in Table 14 and graphically in Figure 4.

TABLE 14.—*Comparative weights of rice plants which were grown in manganese dioxid and calcium carbonate and in calcium carbonate solutions alone, to which were added various amounts of iron as ferrous sulphate.*

Series.	Culture solutions with amount of added material per liter.	Flask No.	Green weight of stalks and leaves.	Oven-dry weight of stalks and leaves.	Oven-dry weight of roots.	Average oven-dry weight.		Condition of plants.
						Stalks and leaves.	Whole plant.	
			Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	
A_1	Sol.+0.005 gm. Fe from $FeSO_4$.	1- 2	13.07	2.69	0.75	--------	--------	Fine, green, healthy.
		3- 4	13.48	2.73	.77	--------	--------	
		5- 6	12.98	2.66	.77	2.69	3.45	
A_2	Sol.+0.005 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 gm. $CaCO_3$.	7- 8	.27	.10	.07	--------	--------	Bleached white; spotted with brown; stunted.
		9-10	.26	.10	.07	--------	--------	
		11-12	.28	.10	.07	.10	.17	
A_3	Sol.+0.005 gm. Fe from $FeSO_4$+0.4 gm. $CaCO_3$.	13-14	.85	.21	.11	--------	--------	Yellowish-white; faint, green, brown spots; little better than A_2.
		15-16	.82	.20	.09	--------	--------	
		17-18	.74	.17	.13	.19	.30	
A_4	Sol.+0.005 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 gm. $CaCO_3$; leaves dipped in 0.5 per cent $FeSO_4$ solution.	19-20	4.29	.80	.31	--------	--------	Green and healthy; dark green spots where iron penetrated.
		21-22	4.30	.88	.32	--------	--------	
		23-24	4.43	.89	.38	.86	1.20	
B_1	Sol.+0.010 gm. Fe from $FeSO_4$.	25-26	12.38	2.62	.75	--------	--------	Green; healthy.
		27-28	14.86	2.76	.86	--------	--------	
		29-30	12.97	2.75	.90	2.71	3.55	
B_2	Sol.+0.010 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 gm. $CaCO_3$.	31-32	.22	.08	.05	--------	--------	Same as A_2; withered.
		33-34	.18	.06	.05	--------	--------	
		35-36	.23	.09	.06	.08	.13	
B_3	Sol.+0.010 gm. Fe from $FeSO_4$+0.4 gm. $CaCO_3$.	37-38	.62	.16	.08	--------	--------	Same as A_3.
		39-40	.81	.20	.09	--------	--------	
		41-42	.83	.21	.10	.19	.28	
B_4	Sol.+0.010 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 gm. $CaCO_3$; leaves dipped in 0.5 per cent $FeSO_4$ solution.	43-44	3.14	.66	.32	--------	--------	Same as A_4.
		45-46	3.66	.71	.30	--------	--------	
		47-48	3.51	.71	.32	.69	1.00	
C_1	Sol.+0.020 gm. Fe from $FeSO_4$.	49-50	14.11	2.71	.88	--------	--------	Green; healthy.
		51-52	13.37	2.64	.82	--------	--------	
		53-54	15.15	2.73	.88	2.69	3.55	
C_2	Sol.+0.020 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 gm. $CaCO_3$.	55-56	.20	.07	.05	--------	--------	Same as B_1.
		57-58	.21	.07	.05	--------	--------	
		59-60	.24	.09	.06	.08	.13	
C_3	Sol.+0.020 gm. Fe from $FeSO_4$+0.4 gm. $CaCO_3$.	61-62	5.00	1.08	.36	--------	--------	Light yellowish-green; somewhat stunted.
		63-64	4.58	.97	.34	--------	--------	
		65-66	5.10	.97	.35	1.01	1.36	
C_4	Sol.+0.020 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 gm. $CaCO_3$; leaves dipped in 0.5 per cent $FeSO_4$ solution.	67-68	1.22	.27	.13	--------	--------	Same as A_4.
		69-70	1.47	.34	.13	--------	--------	
		71-72	1.24	.30	.16	.30	.44	
D_1	Sol.+0.040 gm. Fe from $FeSO_4$.	73-74	11.82	2.60	.87	--------	--------	Green; healthy.
		75-76	12.17	2.97	1.02	--------	--------	
		77-78	12.74	2.74	.86	2.77	3.69	
D_2	Sol.+0.040 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 gm. $CaCO_3$.	79-80	.47	.15	.08	--------	--------	Yellowish-green spotted with brown; stunted.
		81-82	.52	.15	.11	--------	--------	
		83-84	.64	.19	.12	.16	.26	
D_3	Sol.+0.040 gm. Fe from $FeSO_4$+0.4 gm. $CaCO_3$.	85-86	10.68	2.14	.67	--------	--------	Somewhat light in color.
		87-88	11.55	2.31	.67	--------	--------	
		89-90	11.59	2.29	.79	2.25	2.96	
E_1	Sol.+0.080 gm. Fe from $FeSO_4$.	91-92	5.97	1.52	.51	--------	--------	Green; healthy; roots injured by excessive iron.
		93-94	7.24	1.64	.56	--------	--------	
		95-96	5.78	1.45	.50	1.54	2.06	
E_2	Sol.+0.080 gm. Fe from $FeSO_4$+0.4 gm. MnO_2+0.4 $CaCO_3$.	97-98	5.13	1.05	.35	--------	--------	Light green; rather stunted.
		99-100	4.50	1.12	.34	--------	--------	
		101-102	5.32	1.22	.42	1.13	1.50	
E_3	Sol.+0.080 gm. Fe from $FeSO_4$+0.4 gm. $CaCO_3$.	103-104	11.61	2.20	.73	--------	--------	Fine, dark-green plants.
		105-106	12.58	2.52	.72	--------	--------	
		107-108	11.25	2.31	.72	2.34	3.06	

Calcium carbonate with 5 and 10 milligrams per liter of iron supplied from ferrous sulphate caused a strongly chlorotic condition and severe depression in growth. Chlorosis almost disappeared with 20 milligrams and did not occur at all with 40 and 80 milligrams. In fact, with 80 milligrams calcium carbonate caused a decided

increase in growth due to its removal of some of the excessive iron present.

Manganese dioxid and calcium carbonate combined with 5, 10, 20, and 40 milligrams per liter of iron caused a strong chlorosis and a severe depression in growth. The chlorosis was overcome when the leaves were dipped in iron or when the iron supply was increased to 80 milligrams.

Experiments III and VI may be considered together since the plants were grown in each for the same length of time with the same solutions and each had approximately the same check. This has been done in Figure 4. A study of Tables 3 and 6 and Figure 4 indicates that calcium carbonate and manganese dioxid have the same effects. Although the above-mentioned results were obtained when calcium carbonate and manganese dioxid were used singly in excessive amounts, the chlorosis was very greatly increased when the two were used in combination. Manganese dioxid and calcium carbonate each appears to possess its own peculiar chlorotic effect and to exert an additive chlorotic effect in the presence of the other.

Discussion of Results.

The results obtained show that manganous sulphate and manganese dioxid cause a strong chlorosis and a severe depression in the growth of the plant. This chlorosis is overcome when the leaves are dipped in iron solutions or when the amount of iron in the nutrient solution is excessively increased. Manganese thus apparently causes a depression in the assimilation of iron by the plant or a deficiency of iron in the plant. This confirms the results with pineapples previously obtained by the writer. Many investigators have found that manganese, especially in large amounts, causes chlorosis, but none has offered proof to show that manganese-induced chlorosis is due to a depression in the assimilation of iron or to a deficiency of iron in the plant.

Manganese-induced chlorosis occurs in acid solution and is altogether distinct from lime-induced chlorosis which is caused by calcium carbonate. In the latter instance the availability of the iron is reduced by the alkalinity of the solution. Manganese and calcium carbonate can each exert an additive chlorotic effect in the presence of the other.

Since chlorosis is produced by manganese in acid solutions with no excess of lime, it is proved conclusively that chlorosis in general is not due to the alkalinity of the solutions or to excess of lime, but simply to deficiency in iron.

Manganese is commonly referred to as a plant stimulant. In these experiments manganese has been found to cause increased growth only when the solution contained a large excess of iron, some of which the manganese dioxid removed.

AN EXPLANATION OF THE PHYSIOLOGICAL EFFECTS OF MANGANESE ON PLANTS.

Pugliese (*37*) and Tottingham and Beck (*44*) have suspected an antagonism between manganese and iron. In the writer's opinion, however, the physiological effect of manganese, at least the effect of the manganiferous soils, can be explained on purely chemical grounds. Hildebrand (*22*) gives a titration curve for ferrous sulphate in which

the hydrogen-ion concentration of the solution is determined at various stages of titration with sodium hydroxid. Ferrous hydroxid was not precipitated until the solution was made quite alkaline. Ferric salts could not be investigated with the hydrogen electrode, but Hildebrand predicts "that they would behave very much like aluminum salts," which are precipitated while the solution is still

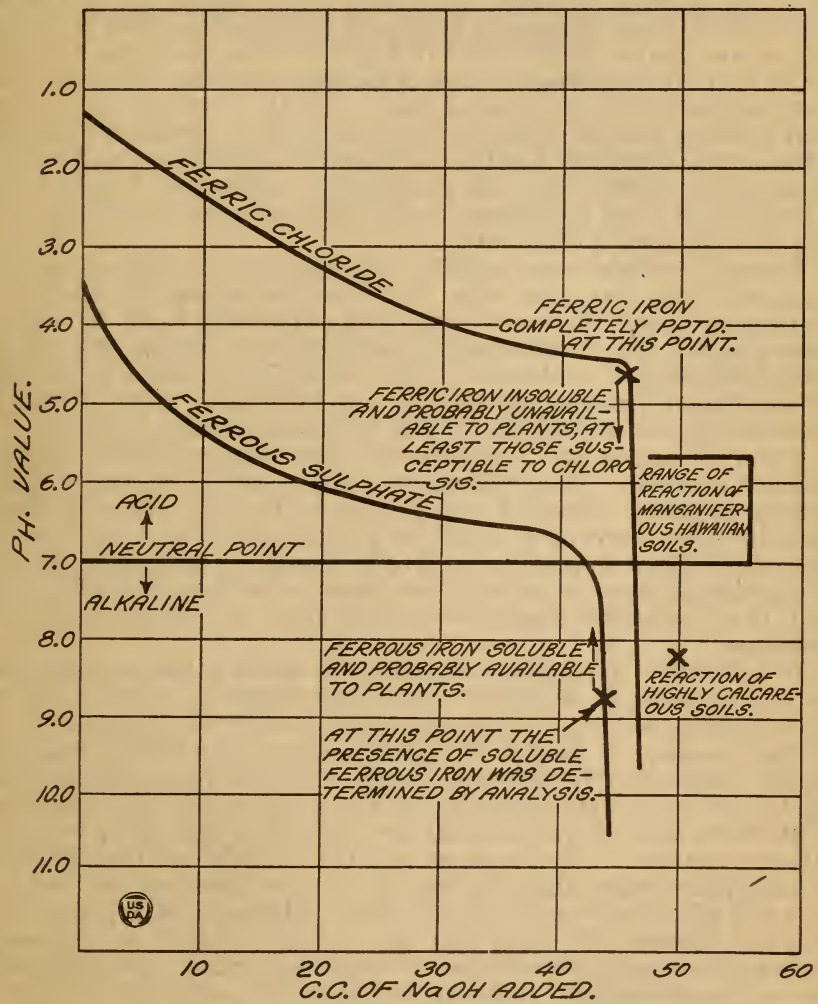

FIG. 5.—Titration curves of ferric and ferrous salts with alkali.

strongly acid. This work of Hildebrand seems to furnish a clue to the manner in which chlorosis is induced.

In order to investigate this more fully the titration curve of ferric chlorid was determined. Various amounts of 0.2N sodium hydroxid were added to 50 cubic centimeter portions of a roughly 0.2N solution of ferric chlorid. The solutions were filtered and the hydrogen-ion concentration of the filtrate was determined by the colorimetric method of Clark and Lubs (*11*). This titration curve for ferric chlorid is given in Figure 5. By careful titration, it was easy to

show that ferric iron was completely precipitated while the solution was still strongly acid because a colorless filtrate could be obtained showing a pH value of about 4.4. No trace of iron could be detected by the sulphocyanate method in this colorless acid filtrate.

Apparently ferric iron is unavailable to many plants on most soils since it is completely precipitated while the solution is still strongly acid and becomes available only when it is reduced to the ferrous form. This would emphasize a hitherto neglected function of humus and organic matter in the soil. In Figure 5 is also given the titration curve for ferrous sulphate. This is not very accurate because oxidation took place during titration, but is chiefly of interest in showing that a strong test for soluble ferrous iron could be obtained when the solution was decidedly alkaline. Although possibly modified by the presence of other ions, this fundamental difference between the solubilities of ferric and ferrous iron throws much light on the manner in which chlorosis is induced.

Figure 5 explains very clearly why chlorosis is induced on the manganiferous Hawaiian soils. In soils containing an excess of manganese dioxid the iron is kept oxidized to the ferric form and, consequently, is not sufficiently available to the plants, at least to those susceptible to chlorosis. Any iron which is added to the soil is immediately rendered unavailable and the effect of such soil then is depression in the assimilation of iron by plants growing on them.

This explanation also applies to the effect of manganese dioxid in nutrient solution. The explanation is not so simple in case of manganous sulphate. Deatrick (*12*) has shown that the brownish-black deposit which forms on the roots of plants that are growing in solutions containing manganous salts is a deposit of manganese dioxid. A like deposit very probably occurs also in the tissues of the plant, and, if so, naturally hinders the assimilation of iron, as previously described.

In addition to explaining the manner in which chlorosis is induced on manganese soils, Figure 5 throws much light on Gile's work on lime-induced chlorosis. Chlorosis will not occur on calcareous soils in the presence of plenty of organic matter or of other material which is capable of furnishing a supply of ferrous iron notwithstanding the fact that oxidation of ferrous iron occurs readily and reduction of the ferric iron to the available ferrous form is difficult in strongly alkaline solutions. This explains why Gile (*15*) did not find chlorosis in pineapples when large amounts of calcium carbonate were added to a soil which was very rich in humus. Moreover, it explains why Gile and Carrero (*20*) found that rice becomes chlorotic in calcareous soils with ordinary percentages of water, but grows normally when the soil is submerged. Reducing conditions of course prevail in submerged soil and ferrous iron is then available to the plant.

The chief problem remaining unsolved in connection with chlorosis is why on the same soil, either manganiferous or calcareous, some plants become chlorotic while others do not. The manner in which susceptible plants become chlorotic has been explained. Plants that are immune apparently obtain sufficient iron for their requirements, either because such requirements are very small or through some special relation of their roots to the soil. It is suggested that those who are interested in this problem grow both susceptible and immune

plants under comparative conditions and in nutrient solutions containing varying amounts of iron and having the availability of the iron diminished by the addition of manganese dioxid or calcium carbonate. The results of such tests should indicate whether plants differ greatly in their iron requirements or whether the resistance to chlorosis is due to some special relation of the plants' roots to the soil.

A SUCCESSFUL TREATMENT FOR THE YELLOWING OF PINEAPPLES ON MANGANIFEROUS SOILS.

RESULTS OF SUPPLYING IRON TO THE PLANTS.

Since the injurious effects of manganese seem to be due simply to a deficiency of iron in the plant, attempts were made to overcome "manganese poisoning" occurring on manganiferous Hawaiian soils by supplying the plants with iron. Experiments were made with the pineapple crop because of its susceptibility to injury and the fact that it is the principal crop of economic importance in the region where the manganese soils occur.

Experiment I.—An effort was made to overcome the toxic effects of the manganese by supplying sulphate of iron and sulphuric acid to the soil in pot experiments. Young pineapple plants which were transferred from a normal soil to a manganese soil to which iron sulphate had been applied gave better results than did plants which were transferred to manganese soil alone.

In a series of pot experiments 25 pounds of manganese soil was used for each pot in which a pineapple plant was grown. Six pots were used as checks. Ferrous sulphate (copperas) was applied to 4 pots at the rate of 500 pounds per acre and to 4 others at the rate of 1,000 pounds per acre. Stable manure at the rate of 12 tons per acre was applied to 4 pots and sulphuric acid (strength 66°) was added at the rate of 1,000 pounds per acre to 2 other pots. Twenty pineapple plants of equal size and appearance were selected from a large number of plants and set in these pots for observation.

The plants in pots to which ferrous sulphate had been added made a slightly better growth at first than did the others. With sulphuric acid a slight stunting was evident in the earlier stages, but in a short time no difference was observed between these and the check plants. Plants in pots to which stable manure was applied were apparently the same as the checks.

At the expiration of five months all of the pineapple plants were fairly uniformly yellow and none of the treatments applied to the soil had any beneficial effect. A solution of iron sulphate was then applied to the leaves of these yellow plants with the result that the normal green color and healthy appearance was restored.

Experiment II.—Experiments on plants in the field were undertaken in cooperation with the Hawaiian Pineapple Co. The leaves of yellow pineapple plants in a field suffering from a severe case of "manganese yellows" were brushed four times at intervals of a week with a 2 per cent solution of iron sulphate. Two weeks after the brushings were completed a striking change was noticeable, and in a month's time the plants had resumed their green color and were making vigorous growth. The condition of the untreated plants adjoining was unchanged. Since then this field has been sprayed

with iron sulphate solution, and all of the plants have made normal growth.

Experiment III.—To show that it is the iron that is effective in restoring the normal green color and health to the plant, and to ascertain the effects of some fertilizing elements in combination with iron, the leaves of very yellow plants were brushed four times at intervals of a week each with various solutions and the condition of the plants was observed one, two, and three months later.

It was observed that the plants which were brushed with a 2 per cent solution of iron sulphate gave results similar to those obtained in Experiment II, and that other plants were not benefited by the application of a pint of the solution to the soil near the roots. The application to the roots of several ounces of iron sulphate crystals was of some benefit, but not nearly so much so as was the application to the leaves of the solution containing a small amount of iron sulphate. No change was noted in plants which were brushed with a 4 per cent solution of sulphuric acid, and very slight change occurred when dilute acid was applied to the soil in quantities of one-half pint and 1 pint per plant. Plants which were brushed with a 2 per cent solution of ferric chlorid (iron chlorid) appeared better than did those which were brushed with iron sulphate, having a fine, dark green color. The chlorid, however, has a tendency to burn the plants. The application of ferric chlorid to the soil was of very little benefit to the plants. The application of a solution of soluble ferric phosphate to the leaves of the pineapple plant was of some benefit, but the application of solutions and crystals to the soil near the roots was of little value. Ferric ammonium sulphate when applied to the leaves in solution and as crystals to the roots was beneficial, but solutions applied to the roots had no effect.

In order to secure, if possible, beneficial action similar to that secured from the use of stable manure, due to solvent action of organic acids, 2 per cent solutions of citric, oxalic, and acetic acids were applied to the soil near the roots of the plants but without noticeable results. It would seem that the temporary beneficial action of the manure is to be ascribed to the growing of the plant in the manure rather than in the manganese soil, as it was necessary to apply large amounts of the manure to the rows. An injection of iron sulphate near the base of yellow plants was of little value.

Sulphuric acid added in quantities of 1 per cent to the iron sulphate solution gave results slightly more beneficial than when iron sulphate alone was used but showed an increased tendency toward burning. A solution containing 4 per cent of ammonium sulphate in addition to the iron sulphate gave beneficial results. Spraying with solutions containing ammonium sulphate in addition to the iron sulphate seems to be of value in that it supplies ammonium salts which are known to be of benefit to pineapples.

From these trials it is evident that the restoration of the normal green color and healthy appearance of the plants is due to the iron which is contained in the iron sulphate solution applied to the leaves. That it is not due to acidity of the salts or the sulphate radical is shown by the unsuccessful results when solutions of sulphuric acid were applied to the leaves.

Experiment IV.—Previous experiments having indicated that the application to the leaves of solutions of iron sulphate alone, of iron

sulphate with acids, and of ferric chlorid (chlorid of iron) is the most practical field treatment for pineapple plants growing on manganese soils, these treatments were compared in a more extensive investigation and the effects of 1, 2, 3, and 4 applications, and of 5 different strengths of the three solutions were observed.

A search in 1918 by C. W. Carpenter (*16*), then station pathologist, having shown the presence of stomata on the underside of the pineapple leaves at the bottom of the grooves of the slightly ridged surface, it was thought that spraying the under surface of the leaves with iron solutions might be more effective than spraying the upper surface of the leaves. Accordingly, an experiment was made in a large field of uniformly yellow plants which were sprayed once a week with iron solutions. The general results of this experiment were judged two months after the first application had been made and were confirmed by observations at other times.

TABLE 15.—*Results of various sprayings of pineapple plants on highly manganiferous soils with solutions of various strengths of iron sulphate, iron sulphate with acids, and ferric chlorid.*

Strength of solution.	Method of application.	Number of applications.	Improvement made by plants treated with—		
			Ferric chlorid.	Iron sulphate.	Iron sulphate + 1 per cent sulphuric acid.
Per cent.					
0.5	Upper	1	Slight	Slight	Slight.
.5	do	2	do	do	Do.
.5	do	3	do	do	Do.
.5	do	4	do	do	Do.
.5	Under	1	do	do	Do.
.5	do	2	do	do	Do.
.5	do	3	do	do	Do.
.5	do	4	Fair	do	Do.
1.0	Upper	1	Slight	do	Do.
1.0	do	2	do	do	Do.
1.0	do	3	do	do	Do.
1.0	do	4	Fair	Fair	Fair.
1.0	Under	1	Slight	Slight	Slight.
1.0	do	2	do	do	Do.
1.0	do	3	Fair	do	Do.
1.0	do	4	do	Fair	Fair.
2.0	Upper	1	Slight	Slight	Slight.
2.0	do	2	Fair	do	Do.
2.0	do	3	do	do	Fair.
2.0	do	4	Green	Fair	Green.
2.0	Under	1	Slight	Slight	Slight.
2.0	do	2	Fair	Fair	Do.
2.0	do	3	do	do	Fair.
2.0	do	4	do	do	Green.
4.0	Upper	1	Slight	Slight	Fair.
4.0	do	2	Fair	Fair	Do.
4.0	do	3	do	do	Green.
4.0	do	4	do	Green	Do.
4.0	Under	1	Slight	Fair	Fair.
4.0	do	2	Fair	do	Green.
4.0	do	3	do	do	Do.
4.0	do	4	Green	Green	Do.
8.0	Upper	1	Slight	Fair	Fair.
8.0	do	2	Fair	do	Green.
8.0	do	3	Green	do	Dark green.
8.0	do	4	Dark green	Green	Do.
8.0	Under	1	Slight	Fair	Fair.
8.0	do	2	Green	Green	Green.
8.0	do	3	do	do	Dark green.
8.0	do	4	Dark green	do	Do.
16.0	Upper	1	do	Fair	Fair.
16.0	do	2	do	Green	Green.
16.0	do	3	do	do	Dark green.
16.0	do	4	do	do	Do.
16.0	Under	1	do	Fair	Fair.
16.0	do	2	do	Green	Green.
16.0	do	3	do	Dark green	Dark green.
16.0	do	4	do	do	Do.

The value of each of these numerous treatments was judged by the average restoration of the green color and the general health and vigor of the plants treated in comparison with the plants in the check rows and with those receiving different treatments. Table 15 gives the results of these treatments.

Table 15 shows that ferric chlorid is not to be recommended for field use. In most cases it was only slightly more effective than iron sulphate, but even a 4 per cent solution burned the plants somewhat. The high cost of ferric chlorid is also a drawback to its use.

The application of iron solutions to the under surface of the leaves gave slightly better results in most instances than did spraying the upper surface, but there was a greater tendency toward burning. The results obtained were not such as would justify, for present large-scale practice, the spraying of plants from below. The addition of acids slightly increased the effectiveness of the iron sulphate but did not prevent burning in some cases.

The most practical, convenient, and economical treatment appeared to be the application to the plants of three or four sprayings of an 8 per cent solution of iron sulphate. A 16 per cent solution was more effective than the latter but burned the plants considerably.

RESULTS OF SOIL TREATMENT.

An experiment was made in cooperation with F. R. Benedict, of Libby, McNeill & Libby, Honolulu, in which flowers of sulphur was applied to a manganese soil in field plats at the rate of 500 to 3,000 pounds per acre. Additions of a red, very acid, upland soil containing apparently considerable quantities of available iron were also made to the manganese soil at the rates of 1 to 6 tons per acre. A third treatment tried was the application to the soil of bagasse soaked in very strong solutions of iron sulphate. None of the treatments was effective, the treated plats yellowing as did the check plats. Even when the solution carried by the bagasse contained 3,000 pounds per acre of iron sulphate no effect was apparent. The yellow plants in this experiment became green rapidly and made vigorous growth when they were sprayed with only a few pounds per acre of iron sulphate in solution. The plants on the sulphur plat showed some stimulation caused by the sulphur.

PRACTICAL TESTS OF THE METHOD OF SPRAYING.

THE SPRAYER USED.

The benefits resulting from spraying yellow pineapple plants on manganese soils with iron solutions were so evident that the cooperating plantation applied this treatment as soon as possible to all of its fields where "manganese yellows" appeared. Check rows only were left unsprayed. As a spraying machine could not easily be secured, a hand sprinkler was used at first with fairly good results. An ingenious modification of the old carbon dioxid orchard spray was devised for the first large-scale treatments of extensive areas. This sprayer was designed by S. T. Hoyt, of the Hawaiian Pineapple Co., and was built at a low cost by the plantation blacksmith. The sprayer is mounted on a single iron wagon wheel, so that turning is easy at the end of the rows. It holds 30 gallons of iron sulphate solution. An ordinary carbonic-acid tank in the rear furnishes pressure

sufficient for spraying. Pipes lead from the rear to the front tank and from the front tank to the spray nozzles, which are placed on the long arm extending crosswise from the sprayer. A gauge on the front tank shows the pressure, which is kept at about 30 to 40 pounds when spraying. (Pl. II, figs. 1 and 2.) As the machine moves forward it sprays four rows at a time. Many complicated sprayers have been tried by the various plantation managers, but the single-wheel type of sprayer, similar to that described above, is satisfactorily used by most of them. The principal modification has been in the use of an air compressor which is driven from the large supporting wheel to furnish the pressure and to take the place of the more expensive carbon-dioxid tank, or the use of a pump similarly driven which delivers the solution from the tanks to the spraying nozzles under pressure.

SPRAYING COSTS.

The cost of spraying is considered negligible in comparison with the expenditures necessary in the raising of pineapples. With the experimental sprayer described above the cost amounted to approximately 60 cents per acre for each spraying. The yearly cost per acre for spraying is not large, since the fields are sprayed on the average only about once a month.

SMALL FIELD TESTS.

All of the fields of the cooperating plantation where "manganese yellow" was evident were sprayed with excellent results. The manganiferous soil had been particularly injurious in one large field of young plants. A sample of the soil from this field, given in Table 2 as No. 636, showed 4.8 per cent of manganese as Mn_3O_4. The plants throughout the field were very yellow and showed no trace of green, while many of the plants which were about six months old had turned brown from the tips of the leaves and were dying. The spraying treatment was applied with immediate benefit, and in six months' time the whole field presented a very vigorous green and healthy appearance.

A 130-acre field was given three sprayings about the time of flowering or later in May and June. This field was not wholly uniform, the plants in some sections appearing slightly affected and in others showing very decided effects from the manganiferous soils. Immediate results were evident when the spraying treatment was applied to the whole field, the plants becoming green and vigorous and the stunted fruit rapidly developing green color and making vigorous growth. The results of analysis of a sample of this soil, taken under the green sprayed plants, show 5.58 per cent of manganese present as Mn_3O_4. (See Table 2, No. 640.) An adjoining unsprayed check row was very yellow and bore small red fruit. The plantation records of this field show an average yield of about 13 tons of fruit per acre.

MAIN FIELD TEST.

The field in which this test was made lies in the Halemanu district of Oahu, where the most highly manganiferous soils occur. The plantings were made on virgin soil to which commercial fertilizer had been applied at the rate of 600 pounds per acre. As the formula for this fertilizer is the property of the cooperating plantation, it can not

be given here, but the condition of the plants in the check rows showed that "manganese yellows" can not be overcome by use of the ordinary fertilizers.

This field was given three sprayings with the experimental sprayer previously described. Some parts of this field were not sprayed until June. So severe were the effects of the manganese that a great number of plants appeared to be destroyed, but a vigorous growth of green suckers as a result of the spraying produced a good ratoon crop.

Part of the field on which this experiment was made was sprayed three times in April. Previous to this the plants had been gone over four times with a hand sprinkler containing a solution of iron sulphate (10 pounds to 50 gallons). Two 300-foot rows were left unsprayed as checks, and two others received only a single spraying with the experimental sprayer. The two rows adjoining the unsprayed rows were held for comparison with them, as in these long rows the effect of any possible variations in the soil is eliminated. Samples of the soil were taken at various places between the two unsprayed rows and likewise between the two sprayed rows. The analyses of these soils, given in Table 2 as Nos. 637 and 638, show 5.19 and 5.12 per cent, respectively, of manganese as Mn_3O_4. A comparison of these analyses of the soils under the unsprayed and sprayed rows, respectively, shows that any difference between them is to be ascribed to the spraying treatment.

The effect of spraying on the stunted red fruit was even more remarkable than that on the yellow plants. These characteristic fruits of manganiferous soils became normal dark green and commenced a most vigorous growth within two or three weeks after they were sprayed. A decided change in them could be noticed within a week. If some of the iron solution struck one side only of an unripe fruit this side became green first and made such growth that the fruit soon presented a "lopsided" appearance. Later the iron appeared to be evenly distributed, because the fruit was fairly symmetrical when ripe.

Plate III, Figure 1, shows the appearance of the unsprayed and sprayed rows on May 19, 1916, about a month after the spraying was done. The view is taken looking north along the rows. The unsprayed row on the left was closest to the camera, but the great improvement in size and appearance of the fruit on the two sprayed rows to the right is evident. It is impossible to show with an ordinary photograph the great difference in color which made the yellow check rows in the green sprayed field visible at a long distance. The rows which received one spraying were quite yellow, but had a greenish tinge compared with the unsprayed rows.

Plate III, Figure 2, shows a view taken halfway along the rows looking south. The unsprayed rows on the right illustrate the variable destructive effects of the manganese soils on the pineapple plant. The two plants in the right foreground set small red fruit which cracked open around the eyes and decayed. Some of the red fruit reaches maturity without decay, but it is of very inferior quality. The third plant visible in the unsprayed row did not blossom at all and was slowly dying when photographed. The plants immediately beyond this suffered the most serious injury, the few dying yellow leaves which were left turning brown and shriveling at the time the

FIG. 1.—FRONT VIEW OF SPRAYER USED.

FIG. 2.—REAR VIEW OF SPRAYER USED.

FIG. 1.—MAIN FIELD EXPERIMENT (MAY 19, 1916). SPRAYED ROWS ON RIGHT; UNSPRAYED ROWS ON LEFT.

FIG. 2.—MAIN FIELD EXPERIMENT (JUNE 30, 1916). SPRAYED ROWS ON LEFT; UNSPRAYED ROWS ON RIGHT.

TYPICAL FRUIT FROM SPRAYED ROWS AND SOME DECAYED FRUIT FROM UNSPRAYED ROWS.

picture was taken. Spraying with iron, however, will induce a growth of green suckers from even such extreme cases as these.

Plate IV shows characteristic fruit from the sprayed and the unsprayed rows. In this and the various field views the broad cylindrical development and filling out of the "shoulder" of the fruit underneath the crown as the result of the spraying from above should be noted. This cylindrical development of the fruit is very much desired by the pineapple canneries because it caused the least waste in sizing for the cans. As a result of this broadening and filling out nearly all of the fruit from the sprayed rows was classed as "first," or No. 1,[6] while most of the elongated fruit from the unsprayed rows, even in the heavier weights, had to be classed as "seconds," or No. 2, the value of which per ton is reckoned as about three-fifths that of No. 1 fruit.

DISCUSSION OF RESULTS.

During June, July, August, and September trips were made once a week or oftener to harvest the fruit as it ripened. After the crown and stem were removed the ripe pineapple fruit was weighed accurately to ounces, and its diameter was carefully measured. The weight of each fruit and its diameter were entered on a large chart according to the position of the bearing plant in the row. Where no fruit was produced the condition of the plant was noted in the chart. Each fruit was classified according to its diameter as No. 1 or No. 2. Where a few fruits had been removed from the sprayed rows before harvesting, the plants were credited with the average of the nearest fruits. A short summary of the yields on the sprayed and unsprayed rows is given in Table 16.

TABLE 16.—*Results of spraying pineapple plants on highly manganiferous soils with iron sulphate solutions.*[a]

	Unsprayed rows.	Rows receiving single spraying.	Rows receiving full iron spray treatment in April.
	Number.	*Number.*	*Number.*
Plants from which fruit was harvested	108	151	244
Plants bearing fruit too young to harvest		5	9
Plants blossoming	3	1	11
Plants starting to blossom			36
Plants dead	31		
Plants with fruit cracked open and decayed	101	81	
Very yellow plants giving no evidence of blossoms	57	62	
Total	300	300	300
Total weight of harvested fruit—pounds	310½	431 1/16	774⅜
Average weight of fruits—do	2¾	2⅞	3 3/16
Fruits harvested	108	151	244
Fruits classed as "first" or No. 1	39	75	214
Fruits classed as "second" or No. 2	69	76	30
Fruits classed as No. 1—per cent	36.1	49.6	87.7
Weight of No. 1 fruit—pounds	128 1/16	250 7/16	700 5/16
Weight of No. 2 fruit—do	181 9/16	181½	74 3/16
Total weight of fruit—do	310¼	431 1/16	774⅜

[6] Cannery classification by diameter, fruits having a diameter above 4¾ inches being classed as No. 1, and those having a diameter of 4¼ to 4¾ inches as No. 2.

[a] These results are for adjoining double 300-foot rows, in each of which there were 150 plants.

Table 16 shows the practical value of the iron-spraying treatment, even though it was not applied until after the plants had suffered during the greater part of their growing period from manganese-induced chlorosis. "Plants starting to blossom" refers to the green, healthy plants on the sprayed rows whose flowering had been delayed by the effects of the manganiferous soil and in which the blossoms was just appearing. Only fruit that was completely destroyed is classed under "Plants with fruits cracked open and decayed." Fruit which showed only a few spots of decay was credited with full weight, although only a part of it could be used. No decay was seen on the rows of fruit which received the full number of sprayings.

Although the increase in the average weight of the fruit was not as large as would be estimated from its appearance in the field, the increase in diameter and size of the fruit on sprayed rows, as mentioned above, caused nearly all of them to class as No. 1, the value of which is considered nearly twice that of the No. 2.

PRACTICAL ADVICE REGARDING THE TREATMENT.

Although beneficial results from an iron-spray treatment, as described above, were obtained with pineapple plants which had suffered during the greater part of their growth from lack of iron, such late spraying is not advised.

Sprayings at intervals of one to four months, depending upon the condition of the plants, are recommended for young crops. The color and general appearance of the plants should be used as an indication of their need of spraying. The plants should be sprayed whenever there is any indication of yellowing or of fading vigor, it being the idea to give them sufficient iron to keep them green and healthy. The exact number and times of sprayings can not be specified exactly for varying local conditions, but the most beneficial treatment for particular fields can easily be ascertained if the color and general vigor of the plant are used as indicators.

The most economical and effective method of supplying the iron sulphate (copperas) appears to be that of spraying the plants with a fairly strong solution in the form of a fine mist. An approximate 6 per cent solution (25 pounds of copperas to 50 gallons of water) has been found very effective in restoring the green color without seriously burning the plants. No injurious effects were noticed even when an application of about 14 gallons of an 8 per cent solution per acre was used in the fine spray on young plants. This solution may have to be weakened when a heavier spray is applied to young plants. Any form of sprayer or even a hand sprinkler may be used provided it applies about 10 pounds per acre of the copperas in solution.

From 3 to 4 per cent (12 to 16 pounds per 50 gallons) of ammonium sulphate in the iron sulphate seems to give good results. It should be remembered that only one of the elements necessary for growth is supplied when the plant is sprayed with iron. Soluble phosphates and nitrogen as sulphate of ammonia or in organic form are recommended for use when commercial fertilizers are to be applied to the soils. Potash is not as necessary in fertilizer formulas for these as for other soils because manganese soils are fairly rich in potash as well as in phosphoric acid and nitrogen and should, therefore, prove fertile when iron is applied to the plants. Cannery ash, which is

used for its potash, should be treated with acids when applied to manganese soils. Nitrate of soda should not be applied to manganese soils because of its injurious effects. The addition of humus-forming materials to the soils is emphasized in every system of agricultural practice. Such materials are of especial value to the soils of Hawaii which are of heavy clay character and have a tendency to puddle. It is recommended that stable manure or other humus-forming material be used if it can be applied at a a reasonable cost. Leguminous green manuring crops are very valuable.[7]

Pineapple plants should be sprayed with iron sulphate solution regardless of the kind of preparation given the manganese soils. No method of preparation of the highly manganiferous soils so far tested allows the plant to absorb sufficient iron and the iron spray should be applied as soon as any signs of yellowing appear.

GENERAL SUMMARY AND CONCLUSIONS.

A review is given of previous investigations on manganese. No conclusive proof is furnished in these of any stimulating action due primarily to manganese. The chlorotic effect found with higher concentrations of manganese has generally been attributed to an indefinite "toxic effect" of the manganese or to "manganese poisoning." It was not proved in these previous investigations that manganese causes a deficiency of iron in the plant or that supplying iron will cure manganese "poisoning."

The writer shows that the manganese of the highly manganiferous Hawaiian soils is present mainly in the dioxid form; that hydrogen-ion determinations indicate these soils to be acid; and that calcium carbonate is absent.

A series of experiments were conducted with rice grown in nutrient solutions to determine the effect of manganous sulphate and manganese dioxid on growth where various amounts of iron were supplied to the nutrient solution from various sources. Preliminary experiments indicated that the effect of manganese depends largely on the amount of iron supplied by the solution.

When the nutrient solution contained a normal amount of iron, manganous sulphate and manganese dioxid caused a strong chlorosis and a severe depression in growth. This chlorosis was overcome when the leaves were dipped in solutions of iron salts or the amount of iron in the nutrient solution was excessively increased.

This manganese-induced chlorosis was thus shown to be due to a depression in the assimilation of iron or to a deficiency of iron in the plant. The previous results and conclusions of the writer concerning the manganiferous Hawaiian soils are thus confirmed.

Manganese-induced chlorosis is altogether distinct from lime-induced chlorosis, due to calcium carbonate, since manganese-induced chlorosis can and usually does occur under acid conditions. Manganese and calcium carbonate can each produce an additive chlorotic effect in the presence of the other.

No evidence was found to show that manganese exerts any stimulating effect on plant growth. With nutrient solutions containing

[7] The value of the different legumes is discussed in Hawaii Sta. Press Bul. 52, Comparative value of legumes as green manure.

an excessive amount of iron, manganese dioxid, by removing some of this harmful iron, caused an increase in growth.

Sodium hydroxid titration curves are given for ferric chlorid and ferrous sulphate. Determination of the solubilities of iron at different hydrogen-ion concentrations show that ferric iron is completely precipitated while the solution is still strongly acid, and that ferrous iron is soluble under fairly alkaline conditions.

This difference in solubility of ferric and ferrous iron affords an explanation of the manner in which manganese induces chlorosis. Manganese dioxid, either present as such or formed from manganous salts, would keep the iron present oxidized to the much more difficultly available ferric form.

A description is given of field experiments in which solutions of iron salts were applied to the leaves of pineapple plants on the manganiferous Hawaiian soils. This treatment effected immediate cure of the "toxic effects" of manganese and induced a normal growth. The treatment was quickly adopted by all the pineapple growers having manganiferous soils and is now being regularly used on considerably over half of the Hawaiian pineapple fields.

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